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METHODOLOGY FOR LONG-TERM PERMEATION TEST PERIODS FOR HD IN HIGH-DENSITY POLYETHYLENE: UNIVERSAL MUNITIONS STORAGE CONTAINER FOR THE NON-STOCKPILE CHEMICAL MATERIEL PROGRAM

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As part of the Explosive Destruction System for the Non-Stockpile Chemical Materiel Program, the Universal Munitions Storage Container was evaluated as a storage candidate for over-packing leaking and non-leaking munitions that contain chemical warfare agents. A 1–2 year storage period was the program target. Permeation experiments were performed with a series of material thicknesses over a 1–3 month period, and thickness versus breakthrough time was extrapolated to the 1–2 year target. Permeation breakthrough measurements for distilled mustard (HD) and non-welded high-density polyethylene (HDPE) at 120 °F were completed for thicknesses of 20–80 mil for extrapolation to the ~250 mil container thickness. A Fick's law extrapolation inferred a breakthrough time of 10–11 days for the 250 mil non-welded HDPE at 120 °F. It is unlikely that a 250 mil thick HDPE container will provide safe containment for the target 1 year period. A custom methodology was developed for the long permeation periods. Expected breakthrough times and, therefore, test times were unknown; thus various permeation times were included in the experimental plan. The methodology developed was successful in providing the necessary measurements. This long-term methodology provides a new capability in permeation cup testing.

15. SUBJECT TERMS

Distilled mustard (HD)	Container	Thickness effect
Chemical warfare agent (CWA)	Fick's law	Thickness uniformity
High-density polyethylene (HDPE)	Permeation	

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PREFACE

The work described in this report was started in July 2013 and completed in July 2014. It was authorized under the Non-Stockpile Chemical Materiel Program, Explosive Destruction System, Universal Munitions Storage Container project.

The use of either trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release.

Acknowledgments

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FOR HD IN HIGH-DENSITY POLYETHYLENE: UNIVERSAL MUNITIONS
STORAGE CONTAINER FOR THE NON-STOCKPILE CHEMICAL
MATERIEL PROGRAM**

1.   INTRODUCTION

At present, the Non-Stockpile Chemical Materiel Program is developing the Explosive Destruction System. The Universal Munitions Storage Container (UMSC) developed by Sandia National Laboratories (Albuquerque, NM) is being evaluated as a candidate for use in over-packing leaking and non-leaking munitions that contain chemical warfare agents (CWAs) in preparation for storage. Leaking munitions must be enclosed in storage containers made of materials that will not allow permeation of CWAs before a specified time and will function properly under a range of temperatures. A methodology for long-term permeation testing is required to support estimation of the maximum safe storage time for CWAs in containers of varying thicknesses. The temperature dependence of permeation is also required to enable extrapolation of the permeation rate to the temperatures that a container may experience in various storage buildings. A storage period of 1–2 years is the program target. Permeation experiments must be performed with a series of lower thicknesses over approximately 1 month to allow extrapolation of material thickness versus breakthrough time to the 1–2 year target for the full container thickness.

This study presented a unique challenge within permeation cell experimentation. Most permeation cell test periods last from several hours to 1 week and are based on protective material requirements. For the UMSC, the desired test period was 1 year. However, only a few months were available for measurements, which was to be followed by extrapolation to 1 year. Given that the typical turnover period for a permeation test system is 1–5 days, the 1 month UMSC study would require the equivalent of 6–30 systems. In addition, most other permeation testing would have to be shut down during this period. The UMSC test would require the dedication of about 100 AVLAG (Aerosol-Vapor-Liquid Assessment Group) permeation cells for a month; this quantity of cells had never been accumulated. The environmental control system could accommodate 12 cells simultaneously. About 100 cells would have to be maintained at the two test temperatures for up to a month. The distilled mustard (HD)-contaminated swatches in the cells would have to be maintained in an independent environmental control system for each temperature and then shuttled into the permeation test system for flux and breakthrough monitoring. Consequently, several safety issues had to be resolved for this storage and transfer process.

The length of time of the permeation period was completely unknown. Furthermore, any feedback on breakthrough time for any material thickness remained unknown until the first data-set measurements were complete. The literature on HD permeation of high-density polyethylene (HDPE) was mostly confined to studies with flexible sheeting of a few mils thickness and test times of less than 1 week. Most results consisted of "no break" at the end of the test period. HD permeation data with 0.25 in. (250 mil) pipe-based containers could not be found. The HDPE material source was primarily pipe-shaped, and swatches required machining

from limited HDPE block material. Therefore, exploratory permeation experiments could not be performed to estimate the thickness values required to generate breakthrough times for an experimental design. There was then no basis for the selection of four thickness values that would produce breakthrough times spread rather evenly over the initial 1 month test period.

A strategy was devised based on an idealized Fick's law model, whereby the thickness versus breakthrough time curve was calculated for a hypothetical 250 mil HDPE material that permeated to breakthrough in exactly 365 days. Although nothing was known regarding the actual HDPE thickness versus HD breakthrough time relationship, it was known that the permeation curve had to be at or above this curve to meet the target container permeation resistance. Conversely, data points measured below this idealized curve would indicate failure to meet the 1 year target. For the available test period of about 1 month, it was possible to select thickness values that would result in breakthrough times that would fall on the idealized curve. For breakthrough times between 2 and 35 days, thickness values of 20, 40, 60, and 80 mil were calculated from the idealized curve, and these thickness values were selected for machining of swatches.

A parallel study was designed for later implementation to directly test the permeation through an HDPE pipe container. This configuration required careful downscaling to minimize the quantity of HD required while maintaining the relevant HDPE-surface to HD-volume ratios.

2.   EXPERIMENTATION

2.1   Test Materials

The container material was composed of Continuum DGDC-2480 BK bimodal polyethylene resin (Dow Chemical Company; Midland, MI). The UMSCs were produced from preformed pipe. The resin was composed of a >99% ethylene/hexene-1 copolymer (Chemical Abstracts Service [CAS] no. 25213-02-9).

The HDPE swatches required custom milling to a size and shape that fit the CWA cells. The welded and non-welded swatches were milled by personnel at Sandia National Laboratories and Innovative Plastic Solutions (Abingdon, MD), respectively. All of the ~3000 thickness measurements on the ~128 swatches were completed and statistically analyzed. Swatches were ranked, and the most uniform swatches were selected for permeation testing. The measurement of HDPE thickness profiles was documented in a separate report (1). Photographs of the permeation specimens are provided in the appendix.

The CWA chemical used in the permeation tests was HD, bis(2-chloroethyl) sulfide; the purity was 95.5 ± 2.8 wt %.

To submit the HD for NMR analysis, 30 µL of neat HD liquid was pipette-transferred into a container and weighed. An internal standard of 1,1,1,2-tetrachloroethane (~20 µL) was added and weighed. A lock solvent ($CDCl_3$) was also added. The mixture was transferred to a Teflon insert, and the insert was closed with a stopper. The insert was then

placed in a 5 mm tube, and the tube was sealed. The tube was analyzed by ^{13}C and ^{1}H NMR for quantization of carbon compounds relative to the internal standard. The HD sample was prepared once and analyzed seven times. The HD purity result was 95.5 ± 2.8 wt %, which was satisfactory for the testing.

The quantity of HD required was an important part of the experimental plan. For the welded specimens, at least 96 mL of HD from a single lot was required, assuming that 1 mL would be placed in each swatch well. Each swatch well would then be 1/4 filled. For the non-welded specimens, rapid permeation was expected based on the breakthrough times of the welded swatches. This allowed for the use of less HD. Each well was spiked with 0.5 mL of HD, which was sufficient to cover the bottom of the well.

2.2　　　　　Custom Permeation Methodology

Modified Glass Permeation Cells. A unique instrument system was required to accommodate the large number of swatches and the potentially long permeation times. A new combination of the glass Q170 cells, the AVLAG permeation system, and the Minicams ChromPerm analytical system (OI Analytical; College Station, TX) was configured. Individual cells passed leak-testing, and the system passed two blank, background tests of several days each.

Modified AVLAG Permeation Cells. The results of the initial permeation test using the glass Q170 cells suggested that the breakthrough times would be short enough to allow simplification of the custom cell system. Because large numbers of cells would not be required for long permeation times, the limited number of AVLAG cells could be employed without preventing further use of the cells and system. A modified method of sealing the AVLAG cells with the machined-well permeation swatches was devised: a flat-ribbed O-ring replaced the rounded O-ring that was ordinarily used, in accordance with TOP 8-2-501A (*2*). The remainder of the procedures were consistent with TOP 8-2-501A, including the leak-check before testing.

2.3　　　　　Environmental Control Procedures

Several custom-built environmental control systems had been developed for the AVLAG permeation system. System 1 was used for the permeation testing. The most detailed documentation was based on System 4, and the procedures from the System 4 manual (*3*) were used. In general, the temperature, humidity, and flow controls were set up the day before the permeation experimentation was performed, and the setup was monitored overnight to ensure stabilization had been achieved. An example of a screen display from the environmental control system is shown in Figure 1. The maximum data storage was about 1 week; therefore, the data file had to be transferred three times: first to a flash drive or equivalent, then to an optical disc, and then to a computer system. For a control sequence longer than 1 week, the files had to be merged within a spreadsheet, and the consolidated data set for the entire permeation experiment was then analyzed.

2.4   Chemical Monitoring System (CMS) Permeation Testing System

The test conditions for the overall permeation testing are summarized in Table 1. The analytical operating conditions are recorded in the screen display in Figure 2. A screen display of a calibration curve is shown in Figure 3.
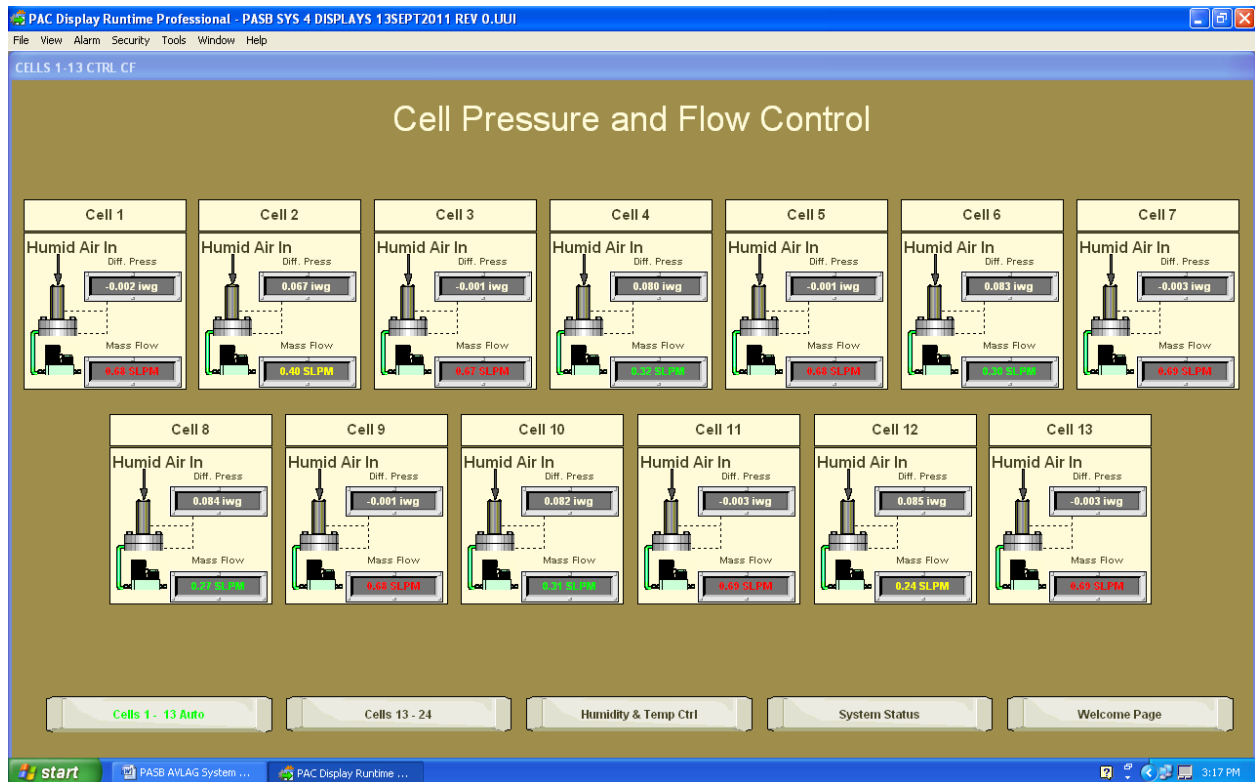
Figure 1. Example of the AVLAG environmental control system screen display for flow control.

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Table 1. Permeation Test Method Summary for HD on HDPE

Test Property	Test Procedure
Test specification	Custom hybrid of Q171 cell and TOP 8-2-501A
Test cell configuration	Static diffusion
Contamination	Welded: 1 mL flooded
	Non-welded: 0.5 mL flooded
Swatch area	9.1 cm^2
Swatch shape	A right circular cylindrical well machined into the swatch
Flow rate under swatch	~300 L/min
Target test period	Unknown, until break
Cell cycle/sampling period	Welded: 3/7 min
	Non-welded: 6/3 min
Stream selection sequence	1 to 12, consecutive
Calibration range	2–100 ng of HD
Cell configuration	Welded: 12 cells total; 5 or 6 replicates per set and 6 negative controls
Gas chromatograph, detector	CMS model 3001 with flame ionization detector
Detection limit	Welded: ~ 0.5 ng × 2; lowest calibration concentration, ~1 ng
	Non-welded: ~1.2 ng × 2; lowest calibration concentration, 2.4 ng

O·I·Analytical

CMS Field Products

Operating Conditions **PAST-1, Single sample** 02:41 04/25/2014

S/N 8397 **RUN NO ALARM**

Method: NGS	Parameter	Setpoint	Actual	Limit
TEMPERATURES, ºC:	Ambient	40	45	± 15
	Inlet	75	75	± 15
	Detector Block	150	147	± 15
	Detector Flame	250	331	± 99
	Column		201	
	Column 1, Low	50	51	± 15
	Column 1, High	200	201	± 15
	Column 1, Rate, ºC/min	200	200	± 30
	Column 2, High	200		
	Column 2, Rate, ºC/min	0		
	PCT Heater		44	
	PCT Heater, Low	40	41	± 20
	PCT Heater, High	250	250	± 30
PRESSURES, psig:	Air	25	27	± 5
	Carrier (Nitrogen)	40	40	± 5
	Hydrogen	25	24	± 5
SAMPLE (2 L/min LMF):	Flow Rate, ccm	50	38	± 99
	Avg. Flow Rate, ccm		32	
	Volume, L @ 21°C, 0 feet		0.0962	
VOLTAGE, VDC:	FPD Photomultiplier	850	850	± 50
ELECTROMETER:	FPD Signal, nA	312	FPD Zero, nA	1000
	-	30	-	1000
TIMED EVENTS, sec:	Purge	0 - 180	Sample	180 - 360
	Desorb	5 - 50	Column 1	40 - 150
	Column 2	150 - 150		

CONCENTRATION REPORTS: **Alarm Setpoint, % ng** 80

Cmpd	Status	Concn, mg/m3	Amount, ng	Height,* nA	Area, nA-sec	RT, sec	Width, sec	Gate On	Gate Off
HD	RUN	0.00	0.00	7	42	139.1	1.1	130	140

* Concentration readings are based on peak height

CALIBRATION INFORMATION:

Cmpd	Det	ng Level	Curve Type	Date/Time	Height,* nA	Area, nA-sec	RT, sec	Width, sec	Gate On	Gate Off
HD	FPD	1.0	Quadratic	04/24/2014 15:46	465	1552	134.2	2.8	130	140

SAMPLING SEQUENCE: **SOFTWARE:** 12012009 **ELAPSED TIME:** 142 sec

Printed :   7/16/2014 12:44 PM   Facility: ECBC (Host 1)   Station: Station 1   Analysis :   38095

Figure 2. Analytical operating conditions for permeation testing of HD and HDPE: non-welded. S/N, serial number; PAST-1, Permeation and Analytical Solutions Branch; and FPD, flame photometric detector.

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Inj No	Delete	Time	Target ng	Height*	Area	RT	Width	Found ng	% Error
1	☐	04/24/14 14:59	1.30	441	1538	133.9	2.9	0.00	100.0
2	☐	04/24/14 15:05	2.60	772	2637	134.0	2.8	2.89	11.3
3	☑	04/24/14 15:11	5.00	246	912	134.2	3.0	0.00	0.0
4	☐	04/24/14 15:23	5.00	1597	5453	134.6	2.9	4.93	1.5
5	☑	04/24/14 15:29	0.00	1170	3874	134.8	2.8	0.00	0.0
6	☐	04/24/14 15:41	10.40	6365	20367	134.2	2.7	10.4	0.0

HD Calibration 10, FPD, 2nd Order - Quadratic
MINICAMS S/N 8397, Station 1, NGS, 04/24/14 15:46

$Ht = C2(Z)^2 + C1(Z) + C0$
$C2 = 6.192E+01 \quad C1 = -7.864E+01 \quad C0 = 4.812E+02 \quad R^2 = 0.99960$

Use the navigation keys to view other calibrations or New to start a new calibration.   Calibration Saved

Figure 3. Calibration of Minicams system for the HD and HDPE swatch
experiments: non-welded.

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3. RESULTS

3.1 AVLAG Temperature Control Results

Examples of the AVLAG temperature and humidity control performance are described in this section.

Figure 4 shows an example of the time versus temperature profile for one of the four temperature measurement and control sites (left, left center, right, and right center). The initial upward temperature spike occurred while the cells were being loaded. For the right-center location, the ~8 °F spike lasted about 7 min. It took about 30 min to cool to near 102 °F, which was the set point for the right-center site. After 1 h, the temperature was near equilibrium.
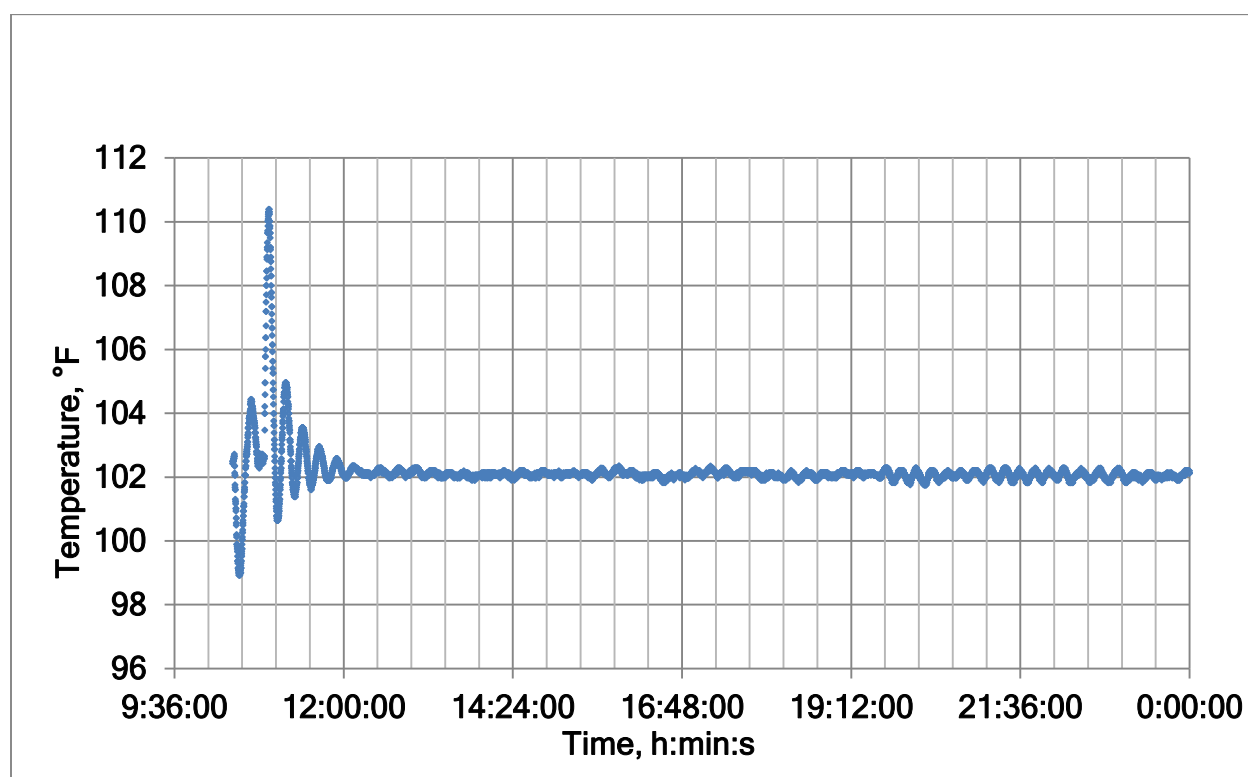
Figure 4. Time vs temperature for AVLAG System 1. Chamber temperature is shown for the right-center location on 05 December 2013. Start time was 1052.

A different time versus temperature profile was recorded for the left side of the chamber and is presented in Figure 5. The downward temperature spike occurred during permeation cell loading and startup. The decrease lasted about 35 min. After 3 h, the left-side temperature was near the set point of 100 °F. Therefore, for shorter permeation experiments, the temperature control system was placed on standby during permeation cell loading, when the chamber doors were opened and closed frequently. For longer permeation times, such as those projected for the container permeation, these initial fluctuations were not significant.

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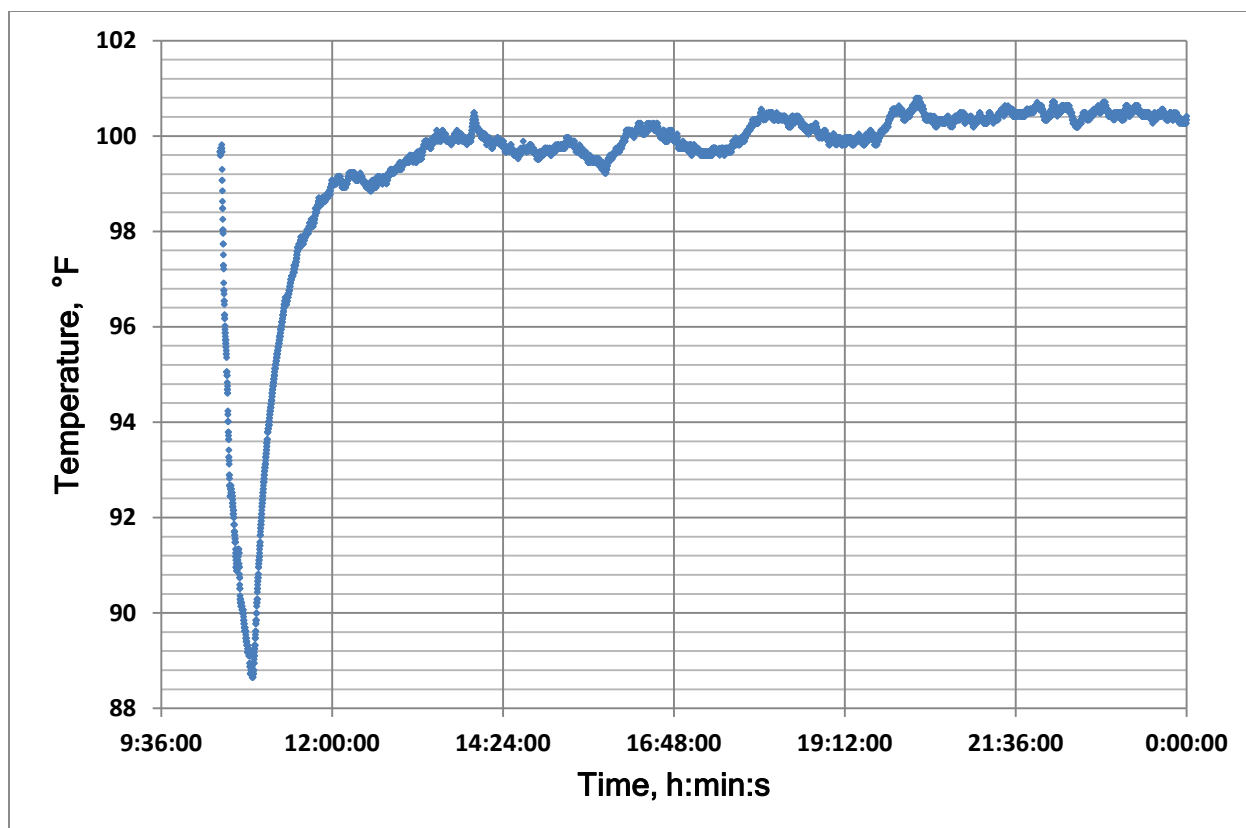
Figure 5. Time vs temperature for AVLAG System 1. Chamber temperature is shown for the left-side location on 05 December 2013. Start time was 1052.

Summary statistics are reported in Table 2 for the temperature and flow rate measurements that describe the control system performance. After the system was closed and equilibrated, the control was very good. The measured temperatures were very close to the targets. Temperatures within the four zones were within 0–2 °F offset from the target, and this offset was required to provide a mean temperature at the target. The 95% confidence intervals (CIs) for the right and right-center locations were three- to fourfold lower than those for the left side; however, all four locations had low variability of 0.076 to 0.036 °F for the 95% CI.

The humidity target of 30% was well-controlled to a mean of 30.8% with a 95% CI of 0.02%.

The flow rates were also well-controlled with a 95% CI of 1×10^{-5} mL/min. Each cell had a unique flow-rate value. These values were input to the analytical calculations; therefore, each cell flow value was taken into account. Overall, the system performance was satisfactory.

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Table 2. AVLAG Environmental Control Performance Summary:
HD on 20 mil HDPE at 100 °F: Welded

Date: 05–06 December 2013 Time: 1025 to 0912		Mean	95% CI	SD	Min	Max
Four temperature positions (°F)		100.2	2.2	1.4	98.9	102.1
Chamber temperature (°F)	Left	99.7	0.025	1.64	88.7	100.9
	Left-center	98.9	0.036	2.34	82.5	100.4
	Right	100.0	0.008	0.50	96.5	106.4
	Right-center	102.1	0.009	0.60	98.4	110.4
Humidity generator temperature (°F)		90.0	0.007	0.48	81.0	95.4
Conditioned air temperature (°F)		90.0	0.006	0.42	87.9	92.2
Humid air manifold temperature (°F)	Left	107.0	0.037	2.39	88.6	108.1
	Right	103.0	0.011	0.72	96.9	103.4
Relative humidity (%)	Left	30.0	0.003	0.21	28.9	32.6
	Right	31.6	0.020	1.34	22.0	33.3
Mass flow controller	Humid air supply	8.6	0.012	0.78	3.6	9.3
	Dilution air supply	16.2	0.012	0.77	15.5	21.2
Flow rate (mL/min)	Cell 1, bottom	0.287	1.5E-06	9.7E-05	0.286	0.288
	Cell 2, bottom	0.301	1.2E-06	7.6E-05	0.300	0.302
	Cell 3, bottom	0.284	4.9E-06	3.2E-04	0.283	0.284
	Cell 4, bottom	0.303	4.5E-06	2.9E-04	0.302	0.304
	Cell 5, bottom	0.253	4.1E-06	2.7E-04	0.253	0.254
	Cell 6, bottom	0.294	7.6E-06	5.0E-04	0.294	0.295
	Cell 7, bottom	0.303	7.0E-06	4.6E-04	0.302	0.306
	Cell 8, bottom	0.314	1.3E-05	8.8E-04	0.311	0.317
	Cell 9, bottom	0.295	7.0E-06	4.6E-04	0.295	0.296
	Cell 10, bottom	0.293	1.0E-05	6.8E-04	0.285	0.300
	Cell 11, bottom	0.293	3.1E-05	2.0E-03	0.240	0.354
	Cell 12, bottom	0.291	7.7E-06	5.0E-04	0.290	0.293

SD, standard deviation.

3.2   Permeation Results for 20 mil HDPE at 100 °F: Welded

The results of permeation testing are summarized in Figure 6. Note that a test temperature change from 120 to 100 °F was required because the sealing wax began to melt at the higher temperature. This change was approved by U.S. Army Chemical Materials Activity.

Given that this was the first test in the series, a number of additional negative and positive controls were configured into the study. The six cells spiked with HD were in positions 1, 3, 5, 7, 8, and 9. The negative-control cells were in positions 2, 4, 6, 11, and 12. Position 10 was configured as an air-monitoring port and was also available for injection of HD as a positive

control. The inlet for position 10 was on the T-junction at the exit of the cell tubing. All curves plateaued at about 0.040 to 0.044 µg/L, which corresponds to the saturation concentration for the detector.

In Figure 6, the elapsed time (in hours) is on the *x* axis, and the HD vapor concentration is on the *y* axis. The cycle time for one cell was 7 min; therefore, the cycle time for all 12 cells was 84 min. Apparent breakthrough occurred at approximately 2–2.5 h for HD cells 5, 7, 8, and 9. Nominal breakthrough was observed for the negative-control cell 6 slightly later, near 3 h. At 4–5 h, nominal breakthrough was recorded for cell 10, the positive-control quality-control (QC) check. Breakthrough results are presented for HD cell 3, then cell 1, at 6–7 h. The negative-control cells 2, 4, 11, and 12 appeared as slowly increasing concentrations, starting around 6–7 h. This appeared to be characteristic of carryover within the stream-selection system and/or the Minicams gas chromatography system.

Three distinct curve shapes can be discerned. A rapid and abrupt increase to saturation within about 2–3 h or about two cycles was observed for HD cells 5, 7, 8, and 9. This shape might be characteristic of defect penetration rather than molecular permeation.

A gradual increase starting at 6 h and reaching saturation at 17–21 h was observed for HD cells 1 and 3. This gradual curve shape appears to be more characteristic of molecular permeation.

Gradual straight-line increases were observed for negative-control cells 2, 4, 11, and 12. These curve shapes might be characteristic of carryover. Results for negative-control cell 6 exhibited an intermediate curve shape that must be characteristic of a breakthrough artifact. Cell 10, an air-monitoring line, showed a gradual increase similar to the carryover negative-control cells 2, 4, 11, and 12, except the concentration level and slope were greater.

A simplistic statement of the results might be that all six HD-HDPE cells experienced breakthrough at 2–6 h. However, the outcome for positive-control cell 6 complicates the interpretation of the results. In addition, because this was the first test in the series, there was an interest in evaluating all possible artifacts and interferences in the permeation configuration before continuing.

Examples of permeation from an individual cell are shown in Figures 7 and 8 for cells 1 and 3, respectively. Mass and flux are plotted on the left and right *y* axes, respectively. The breakthrough time of 6 h is indicated on these plots along with the curve shape for molecular permeation rather than abrupt penetration. An example of rapid breakthrough and flux increase is shown in Figure 9 for cell 5.
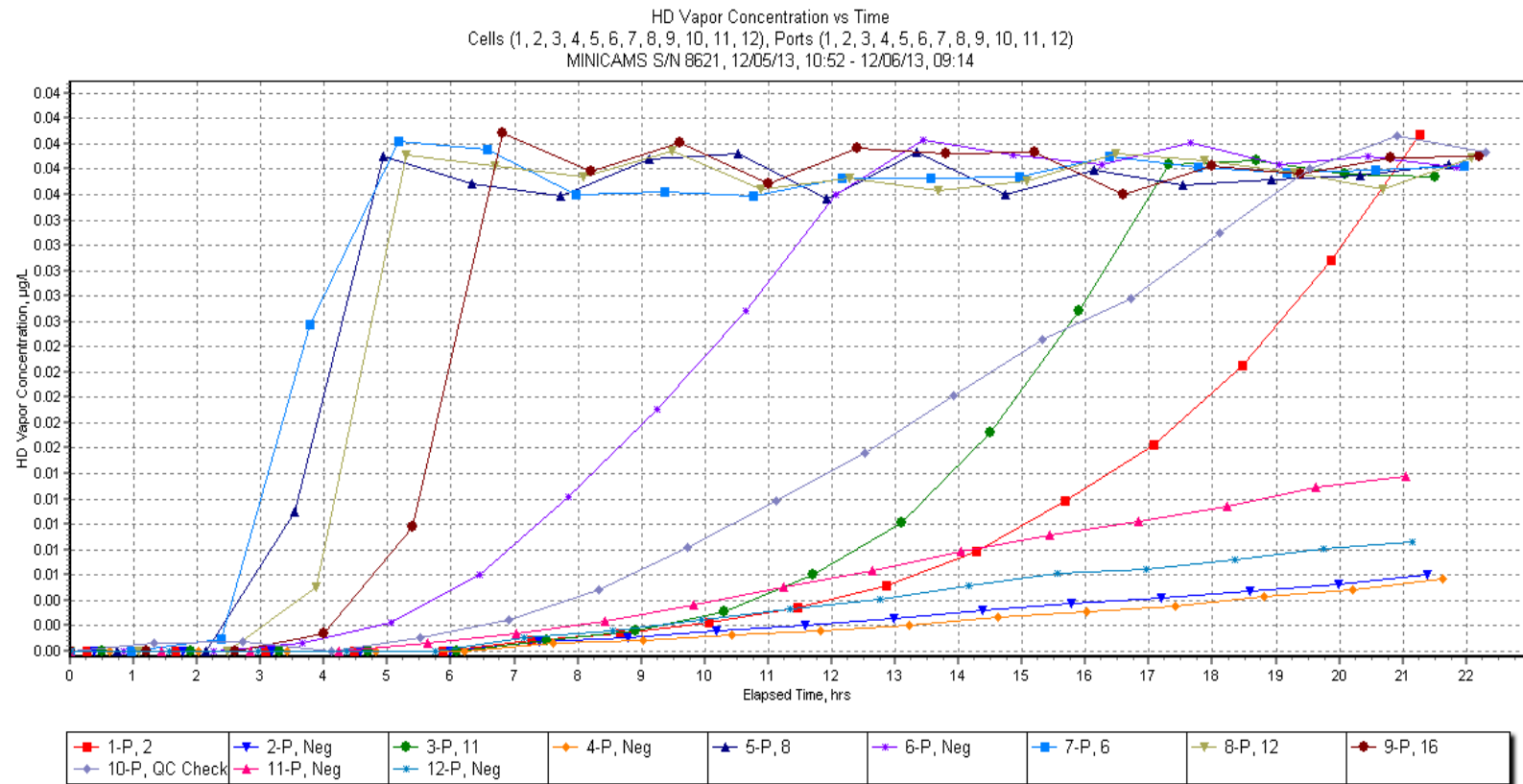
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Figure 6. HD permeation time vs concentration at 100 °F for 20 mil HDPE: welded.
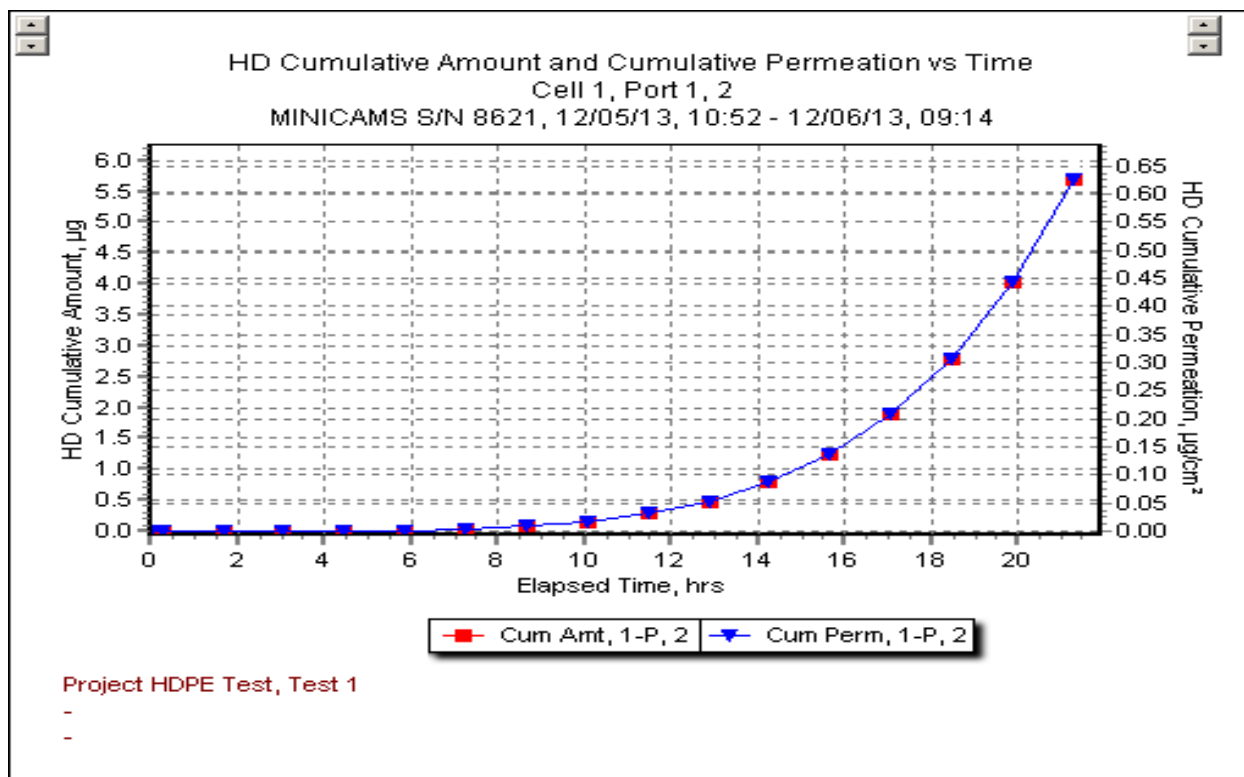
Figure 7. HD permeation time vs cumulative mass for 20 mil HDPE at 100 °F in cell 1: welded.
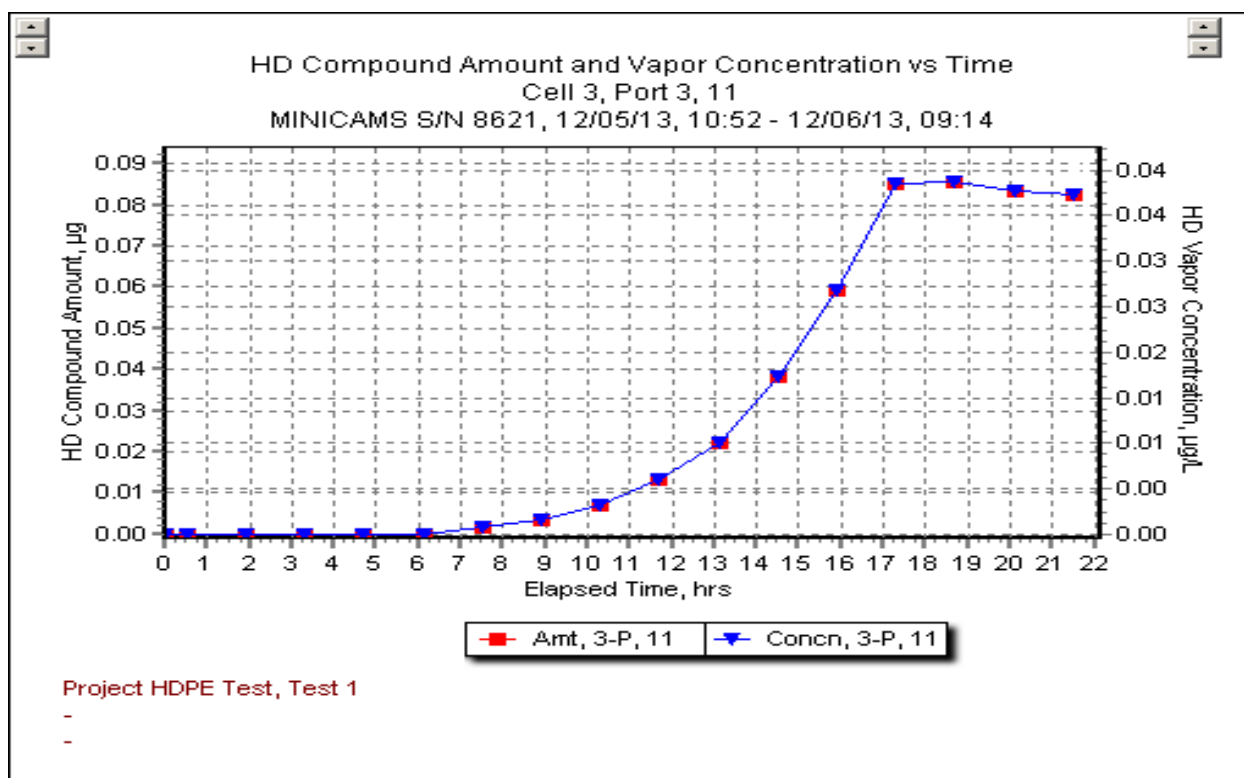

Figure 8. HD permeation time vs cumulative mass for 20 mil HDPE at 100 °F in cell 3: welded.
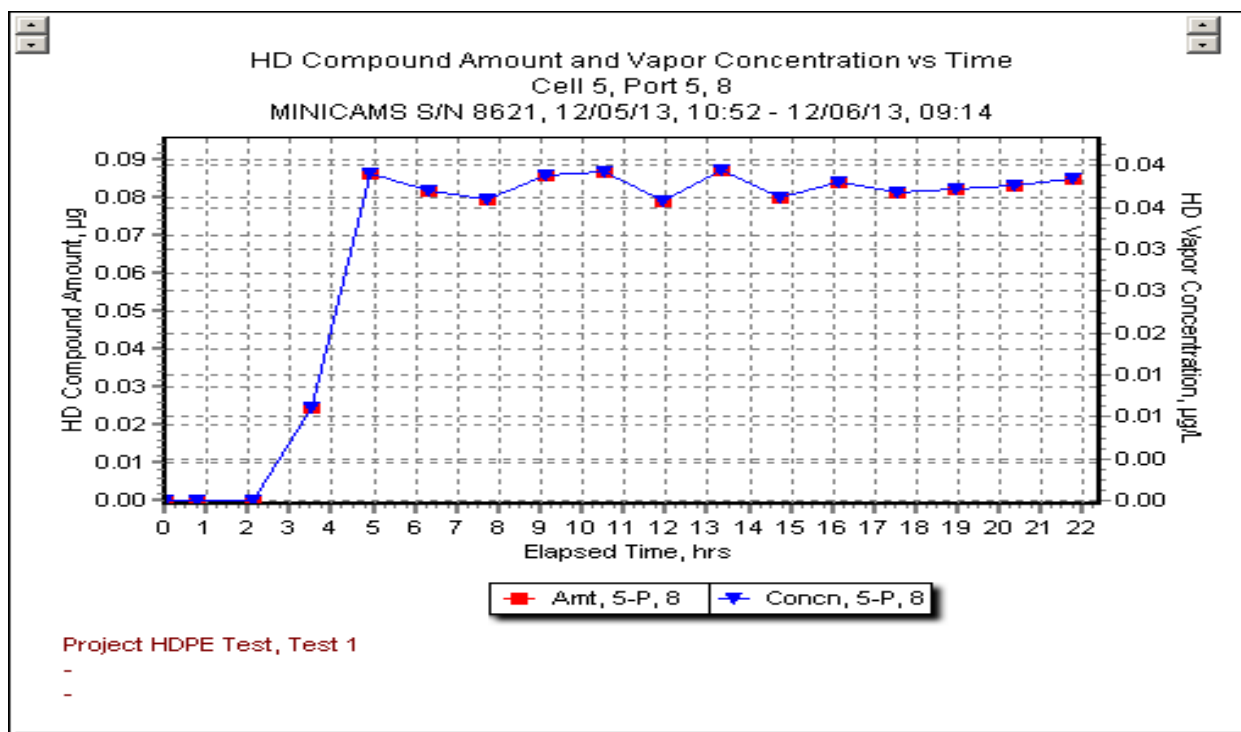
Figure 9. HD permeation time vs cumulative mass for 20 mil HDPE at 100 °F in cell 5: welded.

3.2.1 Confirmation Test: Welded

A standard Q170 test (*4*) of two welded 20 mil HDPE swatches at ~100 °F was performed to confirm the breakthrough as observed by the Minicams system. Two swatches were tested and referenced to a negative control (by C. Gross, Protection Branch, Engineering. Directorate, U.S. Army Edgewood Chemical Biological Center). Breakthrough was observed as color change at 478 and 480 min. Incipient color change was observed at 466 min.

In preparation for visual examination, the swatches were cleaned with isopropanol solvent, which is usually inert with HDPE. No visible loss of integrity was observed. Probing of the weld line with a blunt glass stirrer did not reveal any qualitative defects.

Given the Q170 test results, a breakthrough time of 8 h was assigned to the welded 20 mil swatches at 100 °F. This was in agreement with results for cells 3 and 1: breakthrough occurred at 6 h, and plotted data took the characteristic permeation curve shape.

3.2.2 Comparison of Permeation and Sorption Data

It was interesting to survey sorption correlations with respect to permeation. HD sorption into HDPE was measured previously (*5*), and a plot of time versus weight percent increase in HD is provided in Figure 10 (R^2 is the regression coefficient). Permeation breakthrough occurred at 0.1 to 1 days. Inspection of this sorption curve near the 1 day period shows an approximately 0% net mass increase for duplicate measurements. The sorption method

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used may not have had the sensitivity and low variability required to predict permeation behavior. Significant mean increases in sorption occurred after 50 days, well after breakthrough. An ASTM D543 method (*6*) may have been used to detect sorption as mass per unit area with greater sensitivity.
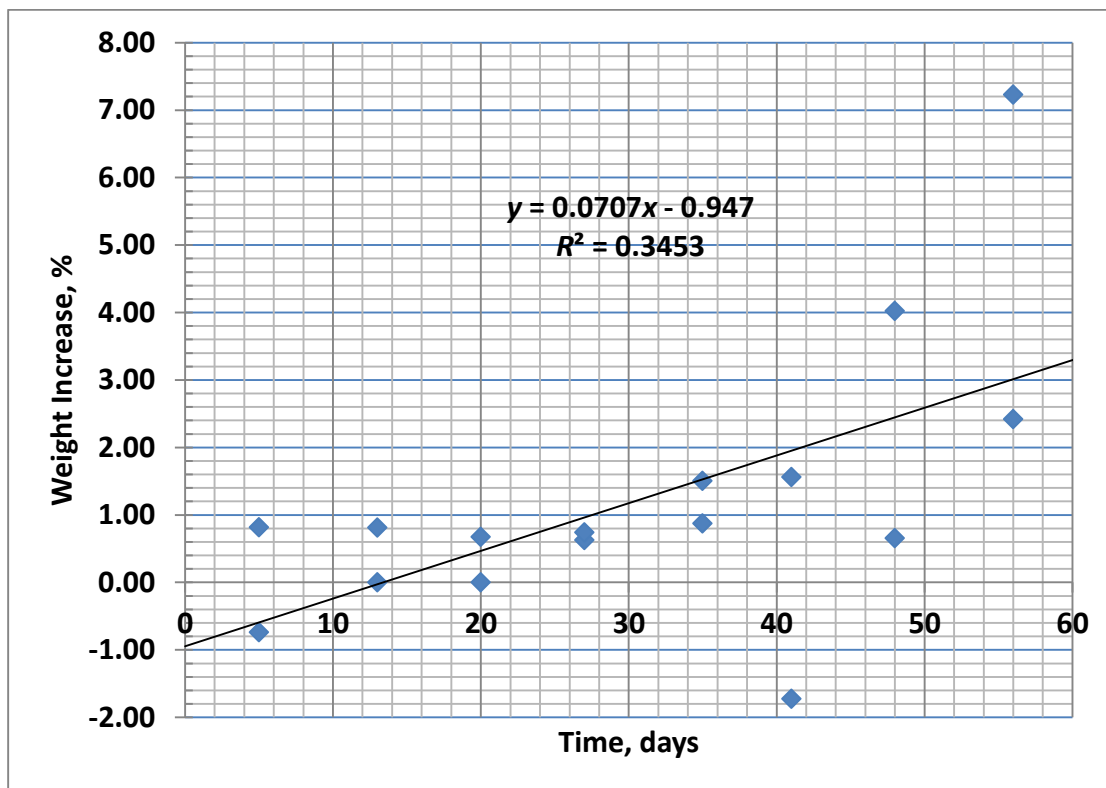
Figure 10. Weight percent increase as a function of time for HD sorption into HDPE: non-zero intercept (*5*): non-welded.

3.2.3　　Breakthrough Time versus Thickness over a Narrow 1.5 mil Range: Welded

Each swatch had a measured thickness, including a thickness profile that identified the minimum thickness. In Figure 11, the minimum thickness for each swatch is plotted versus breakthrough time over this narrow range of 1.5 mil. The expected positive correlation is shown; however, given the correlation coefficient, it is not significant. The intent was to correlate minimum thickness over the 20–80 mil range rather than only for this 18.3–19.8 mil range. The correlation would be expected to increase over this larger range.

Figure 11. Minimum thickness vs permeation breakthrough time for HD and 20 mil HDPE over an HDPE thickness span of 1.5 mil: non-welded.

3.2.4 Summary for 20 mil HDPE at 100 °F: Welded

HD appeared to permeate the welded 20 mil HDPE swatches at 100 °F after about 6–8 h. Based on curve shapes, the breakthrough was at 6 h for the AVLAG system cells 1 and 3. The breakthrough was confirmed through the use of two independent permeation methods.
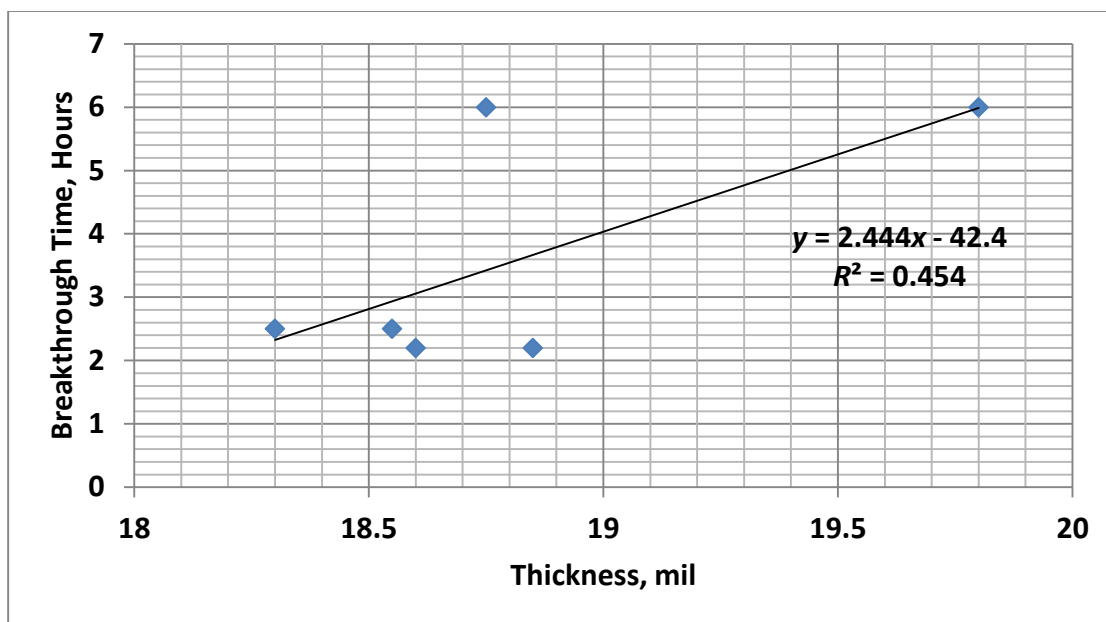
The custom combination of the glass QC cells, the AVLAG permeation system, and the Minicams ChromPerm analytical system performed adequately during the initial test. However, the relatively large quantity of HD present combined with the highly sensitive detection protocol requires the use of an extensive negative-control strategy as well as leak-free couplings.

Test Method 204, which is known as the Q170 test (*4*), is a useful confirmation method. The method may be limited to permeation test periods of only 8–10 h (or 1 working day) because of facility and scheduling restrictions.

3.3 Permeation Results for HDPE at 120 °F: Non-Welded

Based on the relatively short breakthrough times identified in the welded HDPE permeation experiments, the procedures were simplified with the expectation of continued short breakthrough times. The procedures were based on the use of a single AVLAG cell, to eliminate the possibility of cross-contamination among cells. A flat-ribbed O-ring was used to seal the swatches, replacing the wax sealing procedure. This change allowed for the temperature to be returned to 120 °F, which is the preferred high-temperature test condition. The limited ChromLink data acquisition system (OI Analytical) was employed rather than the fully

functional ChromPerm system that was used for the welded HDPE experiments. The deposition or spike time was estimated on the basis of an offset from the calibration check injection time for specimens 14-04-02 and 14-04-29.

Several recognized criteria exist for assigning breakthrough time. The criterion based on cumulative flux, which can be appropriately applied to most dermal protective clothing, is not appropriate for assessing the hazard from breakthrough of a munitions container in an enclosed storage room. The CWA concentration that is hazardous as a vapor leak can be quite low for eye injury and respiratory effects. The ASTM criterion based on minimum detection concentration is useful for data that is not noisy. An extrapolation to a zero concentration intercept is also used in chemical-material permeation research, and this is the technique applied to these data sets.

The plots of the overall permeation curves for the five experiments are presented in Figures 12–21. The plots of the extrapolation to zero mass are also shown for each experiment. Only the time increments from HD deposition are shown because the elapsed-time calculation generates negative times for earlier intervals. The mass of HD (in nanograms) sampled and detected by the analytical system was employed as raw data indicating permeation; it was not converted to a mass permeated during the entire 3 min of sampling or to a flux based on the full sampling time and swatch area. Likewise, the time reported was the time at the end of the sampling period; it was not adjusted to the midpoint of the sampling period. This only accounted for a 1.5 min offset. In all of the permeation curves, the mass of HD plateaued at about 35–50 ng due to saturation of the detector; therefore, this was not a steady-state permeation rate that indicated permeation had reached an equilibrium.

3.3.1　　Mass versus Time Permeation Plots for 20 mil HDPE and HD: Non-Welded

The mass of HD permeated versus the elapsed time from the HD deposition or spike is plotted in Figure 12 for the nominal 20 mil HDPE permeation specimen. The mass appeared to reach saturation at 130 min and then exhibited an unusual decrease before returning to saturation mass levels of 42–50 ng. Therefore, the data points between 140 and 190 min seemed to fall within the saturated detector region of the curve. There was a problem with the analytical system during that period; however, the problem occurred after breakthrough and did not influence the results. An obvious extrapolation to zero mass was indicated for the data between 90 and 120 min. An alternate and more conservative breakthrough time might be assigned using the data around 60–80 min. The curve shape is not clearly that of molecular permeation, and it might be characteristic of defect-controlled penetration. The permeation period before saturation was between 90 and 130 min or 40 min, which was about 40% of the lag time. Because detector saturation cut short the permeation period, the permeation period was actually even longer; this argues for the assignment of permeation rather than defect penetration.

The extrapolation to zero mass using the data obtained between 88 and 120 min is reported in Figure 13. The intercept provides a breakthrough time estimate of 89 min.
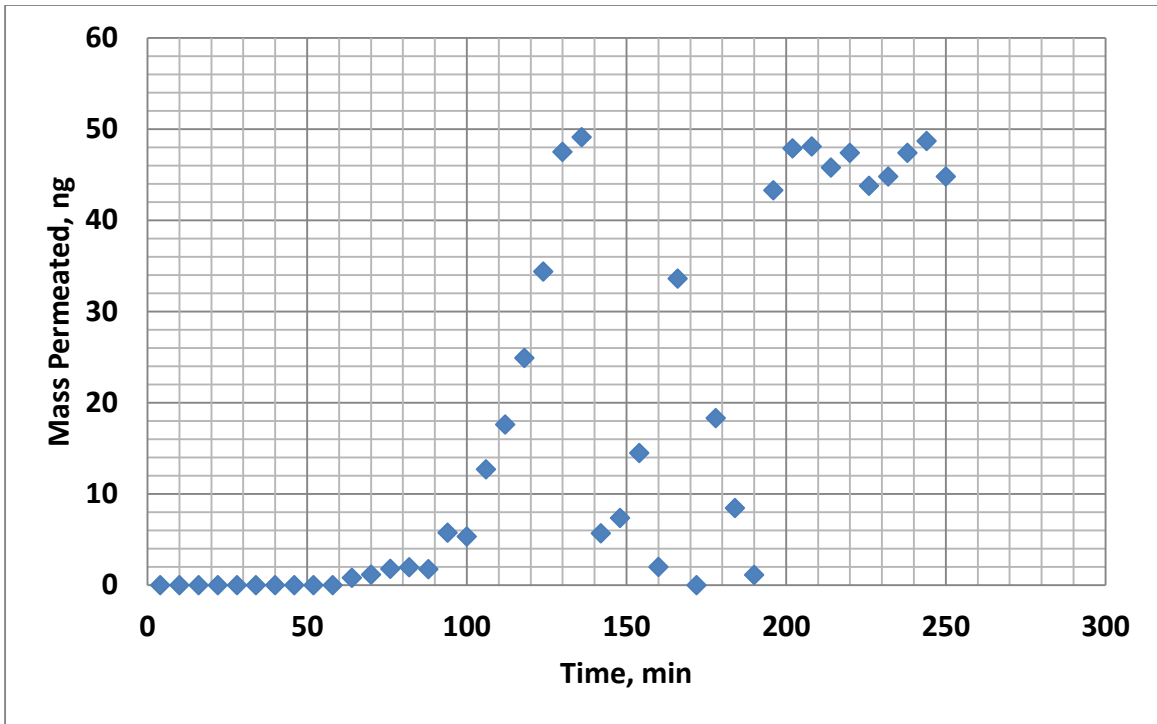
Figure 12. HD breakthrough time vs mass permeated for 20 mil HDPE at 120 °F; specimen 14-04-02: non-welded.
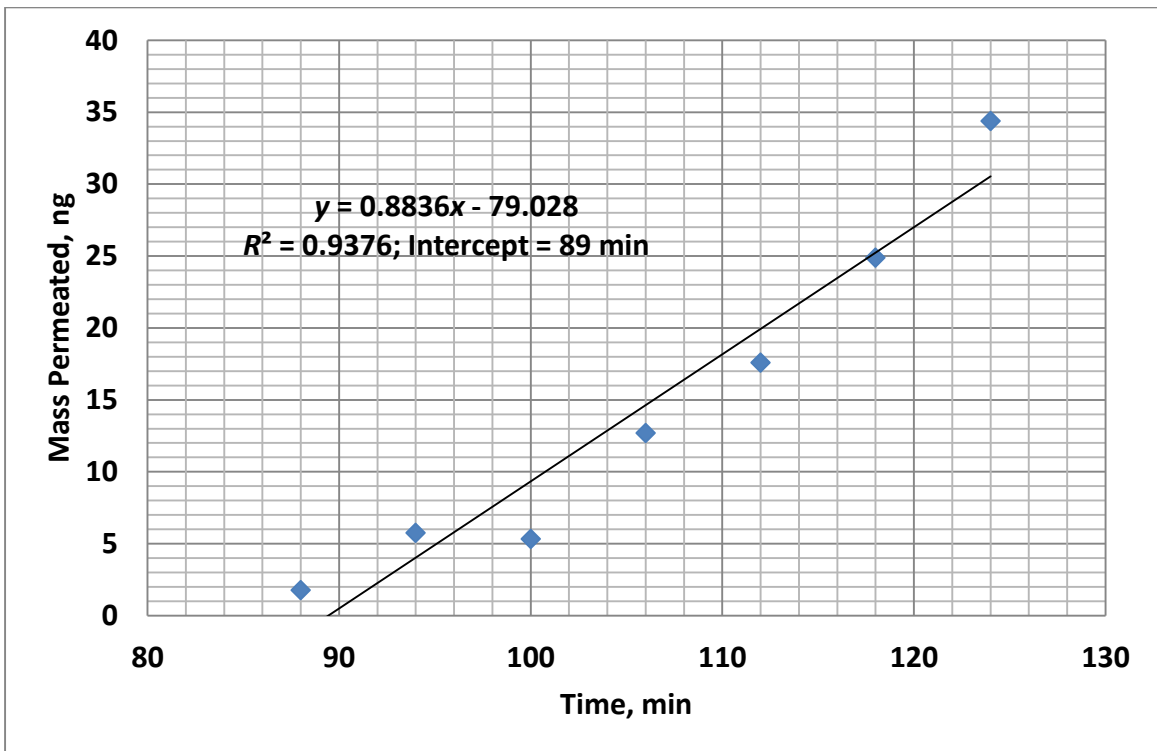

Figure 13. HD breakthrough time extrapolation from time vs mass permeated data for 20 mil HDPE at 120 °F; specimen 14-04-02: non-welded.

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3.3.2   Mass versus Time Permeation Plots for 40 mil HDPE and HD: Non-Welded

The mass of HD versus the elapsed time from the HD deposition is presented in Figure 14 for the nominal 40 mil HDPE permeation specimen. The mass appeared to reach saturation at 540 min. The curve shape is not that of molecular permeation and appears to be characteristic of defect-controlled penetration: the HD mass jumped from 2–4 to 50 ng saturation in only 12 min, which was only 2–3% of the overall lag time.

The extrapolation to zero mass using the data obtained between 530 and 544 min is reported in Figure 15. The intercept provides a breakthrough time estimate of 530 min.
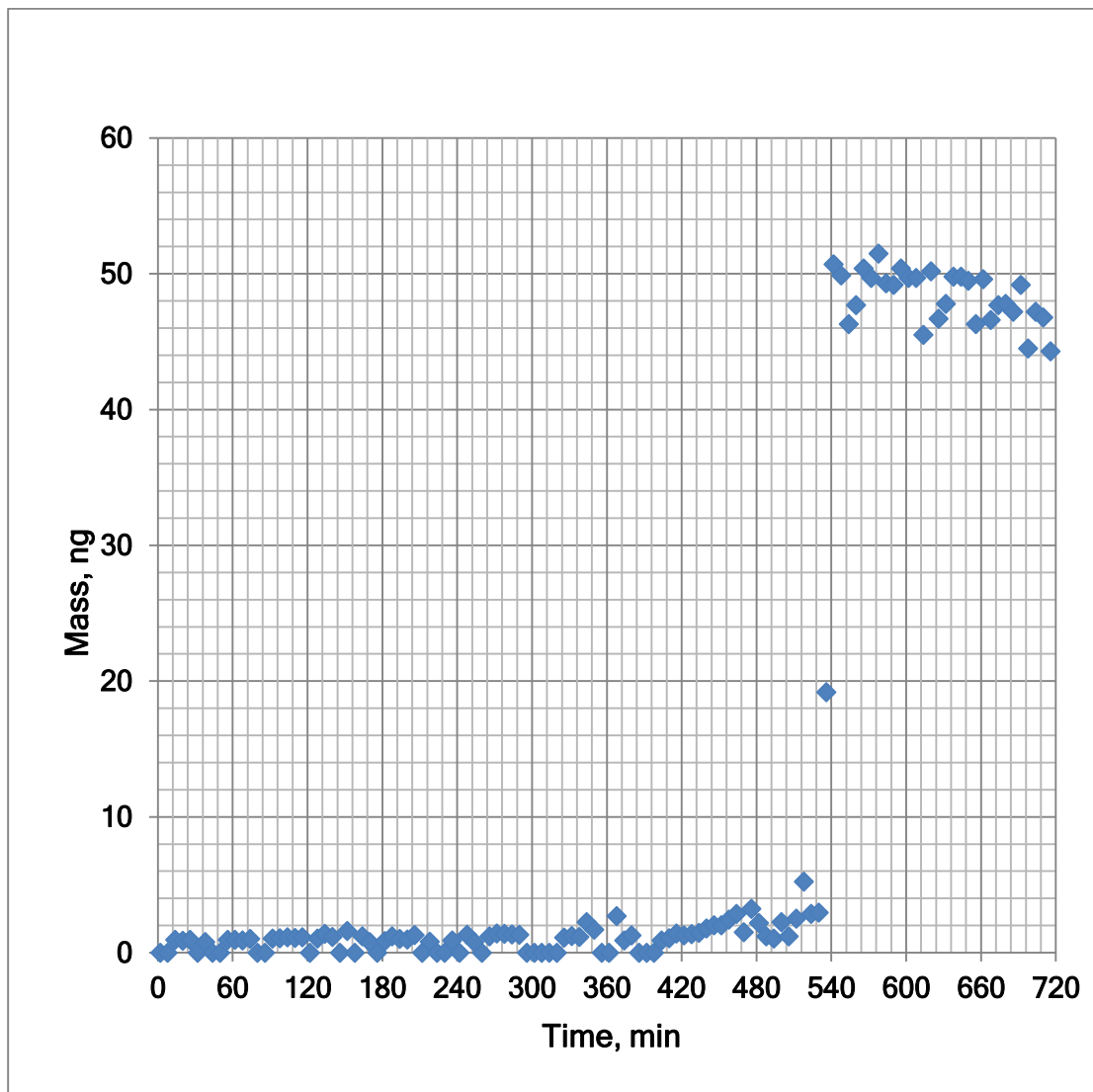

Figure 14. Time vs HD mass permeated for 40 mil HDPE at 120 °F; specimen 14-04-09: non-welded.
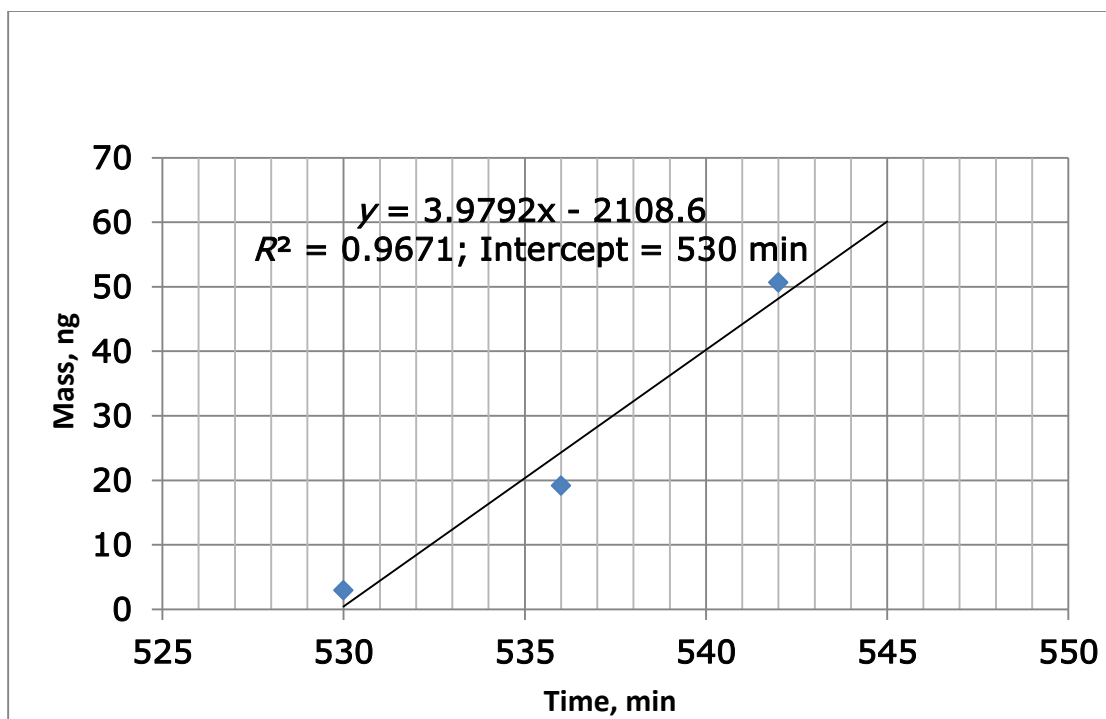
Figure 15. HD breakthrough time extrapolation from time vs mass permeated data for 40 mil HDPE at 120 °F; specimen 14-04-09: non-welded.

3.3.3 Mass versus Time Permeation Plots for 60 mil HDPE and HD: Non-Welded

The mass of HD versus the elapsed time after the HD spike is plotted in Figure 16 for the nominal 60 mil HDPE permeation specimen. The mass reached saturation at about 1300 min. The elongated curve shape is characteristic of simple molecular permeation. The HD mass gradually increased from 720 to 1300 min at saturation over a period of 500 min. Although it is clear that the breakthrough time was about 720 min, the noisy baseline makes it problematic to assign an exact time. The baseline increased at about 480–500 min and stabilized at around 0.8–0.9 ng of HD. Therefore, rather than extrapolating to zero mass of HD, a regression line was established at the new baseline, and a second regression line was calculated for the increasing HD concentration. The results are plotted in Figure 17. The baseline regression has a slight slope, but it was useful in defining the offset baseline. The permeation regression line between 740 and 780 min produced a small but significant slope with a correlation coefficient of 0.966. The two regression lines intersect at about 740 min, and this was assigned to be the estimated breakthrough time.
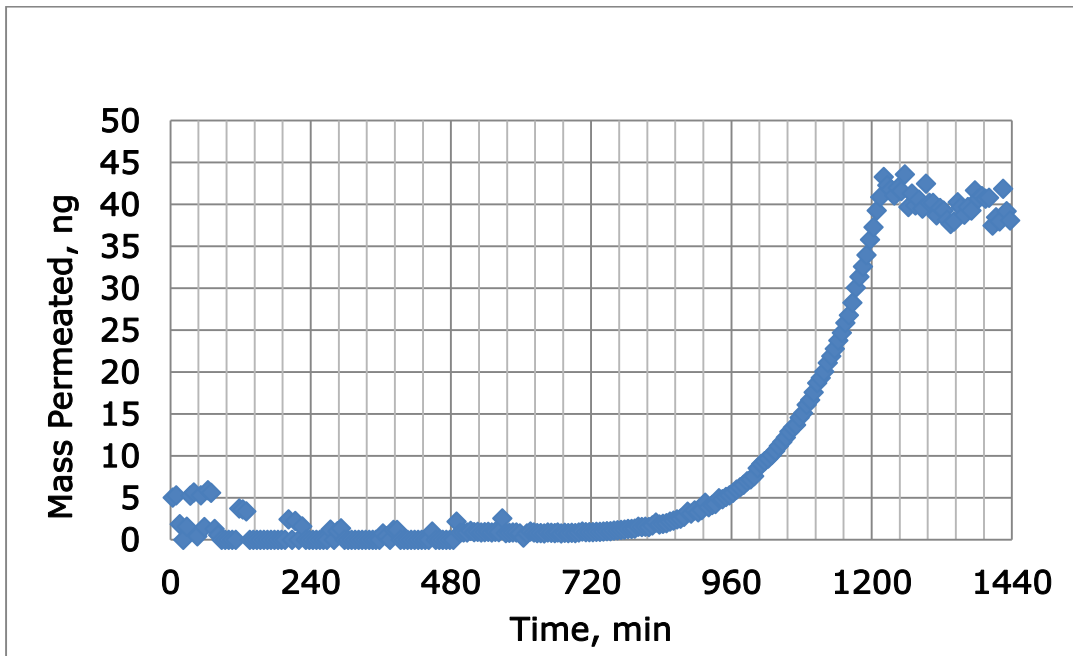
Figure 16. Time vs HD mass permeated for 60 mil HDPE at 120 °F; specimen 14-04-29: non-welded.
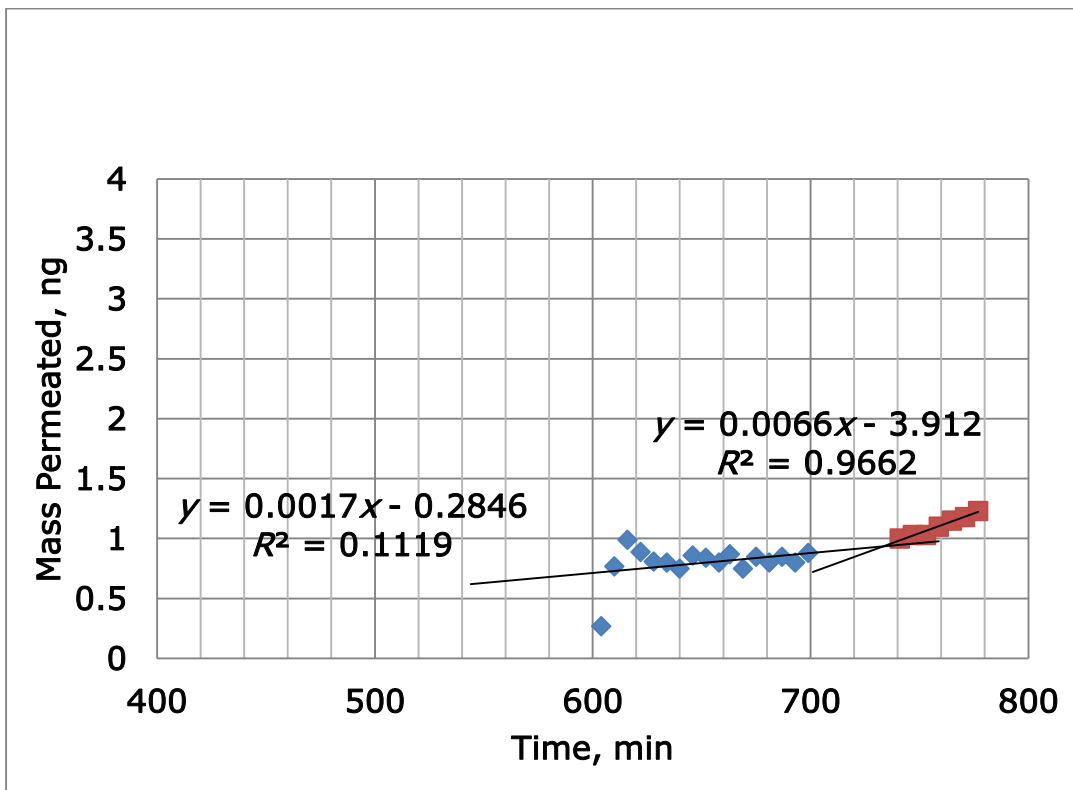

Figure 17. Time vs HD mass permeated for 60 mil HDPE at 120 °F; specimen 14-04-29: non-welded. Regression lines intersect at about 740 min.

3.3.4 Mass versus Time Permeation Plots for 80 mil HDPE and HD: Non-Welded

3.3.4.1 Specimen 14-04-15: Non-Welded

Two 80 mil HDPE specimens were tested, and they are discussed separately. The mass of HD versus the elapsed time after the HD spike is plotted in Figure 18 for the nominal 80 mil HDPE permeation specimen 14-04-15. The curve shape indicates molecular permeation. The HD mass gradually increased from 1200 to 1400 min to 2600 min at saturation over a period of 1200 min. The breakthrough time was about 1300 min. There are two parallel baselines, one at 0 ng and the other at about 0.8 ng of HD. The increase in mass and permeation appears to have occurred from the higher (0.8 ng) baseline. See Figure 19 for an expanded view of the baseline. Rather than extrapolating to zero mass HD, a regression line was established at the 0.8 ng baseline, and a second regression line was again calculated for the increasing HD concentration. The results are plotted in Figure 20. The baseline regression has a near-zero slope and defined the offset baseline. The permeation regression line between 1400 and 1600 min yielded a significant slope with a correlation coefficient of 0.98. The two regression lines intersect at about 1330–1340 min. By coincidence, the last zero mass HD value was at 1329 min; therefore, this was assigned to be the estimated breakthrough time.

Figure 18. HD breakthrough time vs mass permeated for 80 mil HDPE at 120 °F; specimen 14-04-15: non-welded.

Figure 19. HD breakthrough time vs mass permeated for 80 mil HDPE at 120 °F; specimen 14-04-15, with expanded baseline resolution: non-welded.
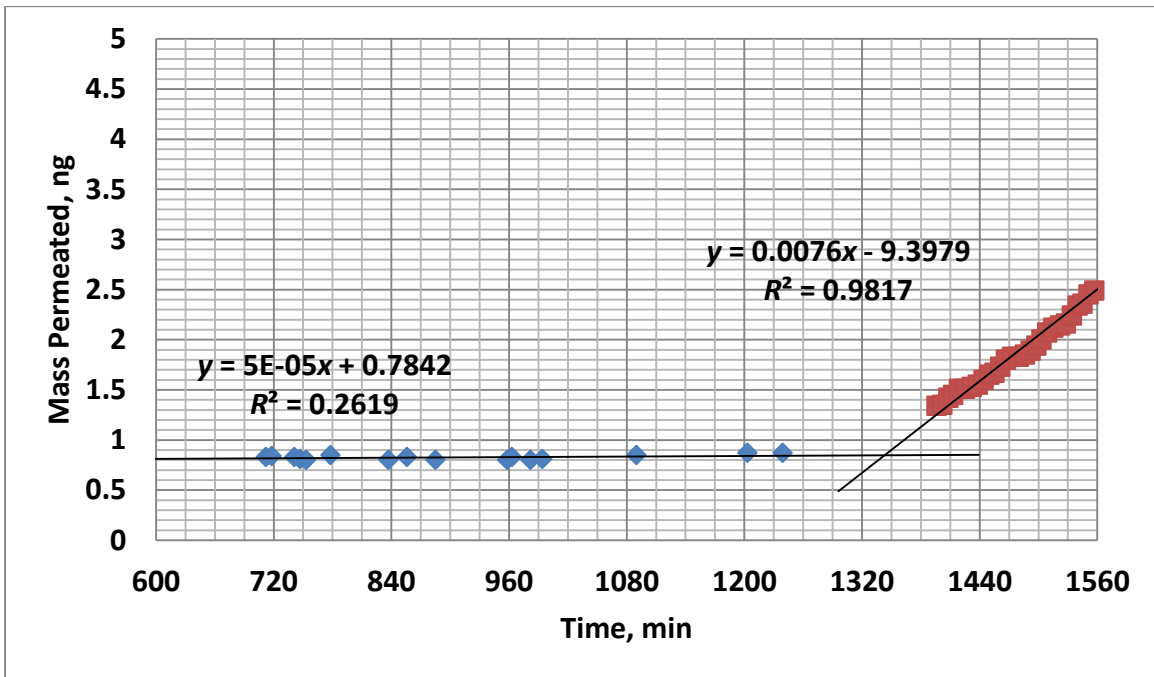
Figure 20. Time vs HD mass permeation for 80 mil HDPE at 120 °F; specimen 14-04-15: non-welded. Regression lines intersect at about 1330–1340 min.

3.3.4.2 Specimen 14-04-25: Non-Welded

The mass of HD versus the elapsed time after the HD spike is plotted in Figure 21 for the nominal 80 mil HDPE permeation specimen 14-04-25. The curve shape suggests molecular permeation. The HD mass slowly increased from 1700 to 2500–2600 min at detector saturation over a period of 800 min. The breakthrough time was about 1700 min. The permeation regression line between 1720 and 1760 min yielded a slope with a correlation coefficient of 0.95. The intercept was 1720 min, and this was taken as the breakthrough time (see Figure 22).
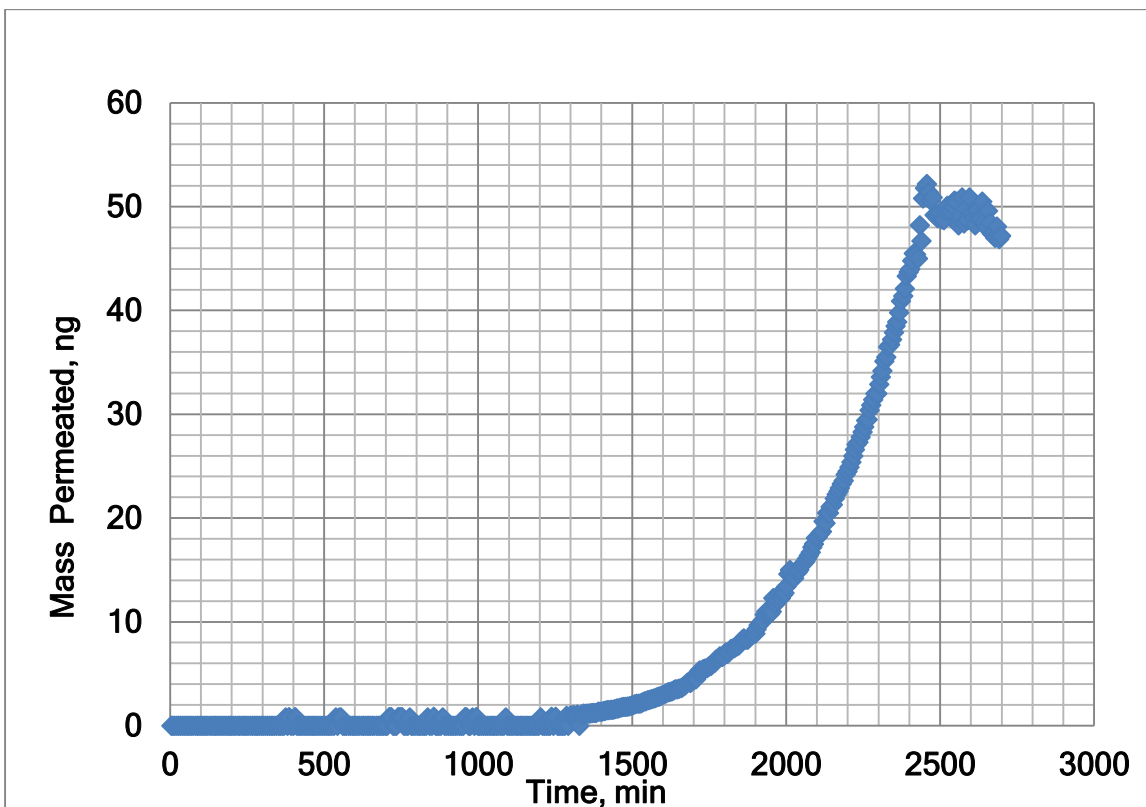

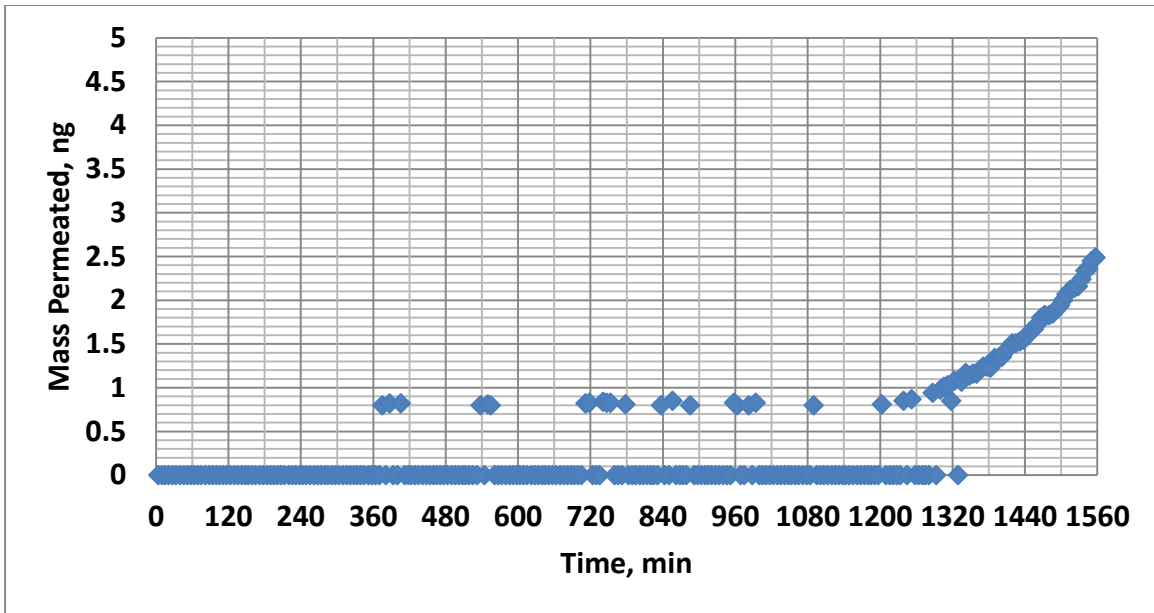Figure 21. HD breakthrough time vs mass permeated for 80 mil HDPE at 120 °F; specimen 14-04-25: non-welded.
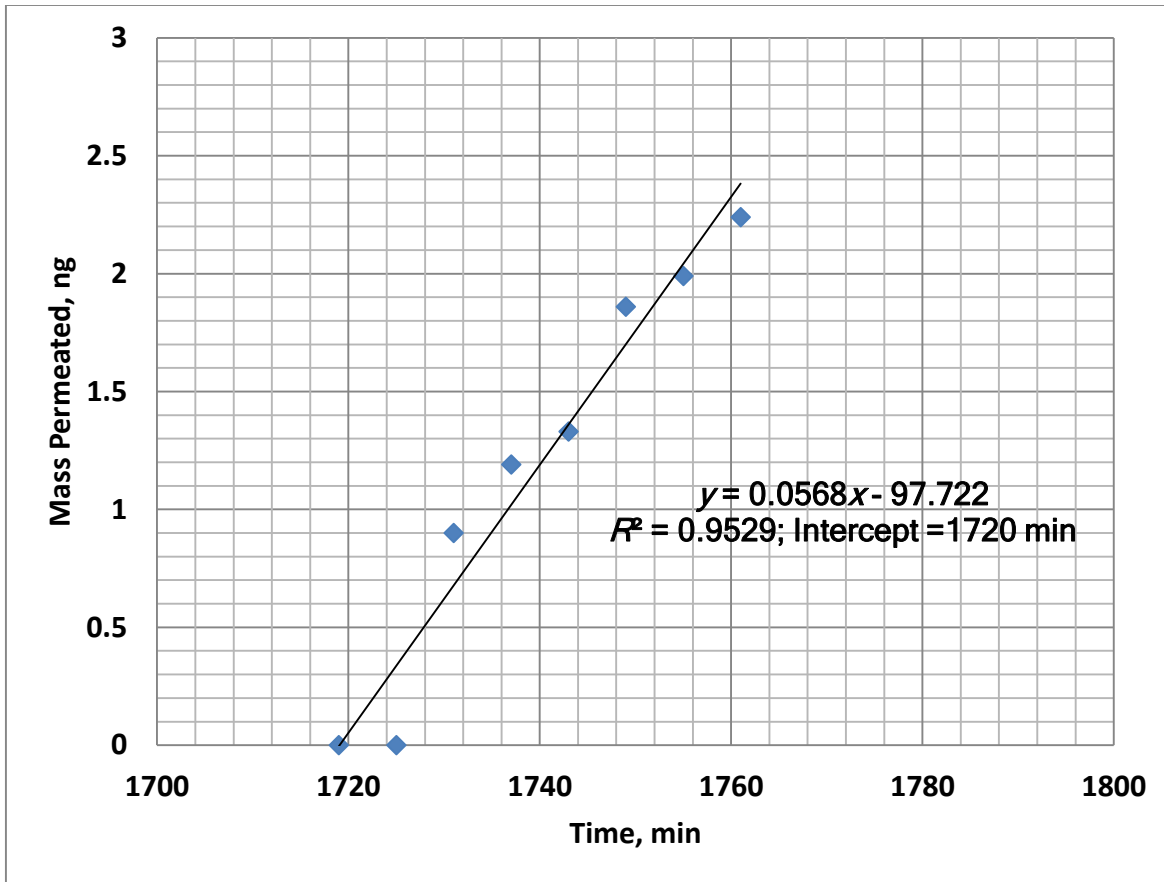
Figure 22. HD breakthrough time vs mass permeated for 80 mil HDPE at 120 °F;
specimen 14-04-25, with expanded baseline resolution: non-welded.
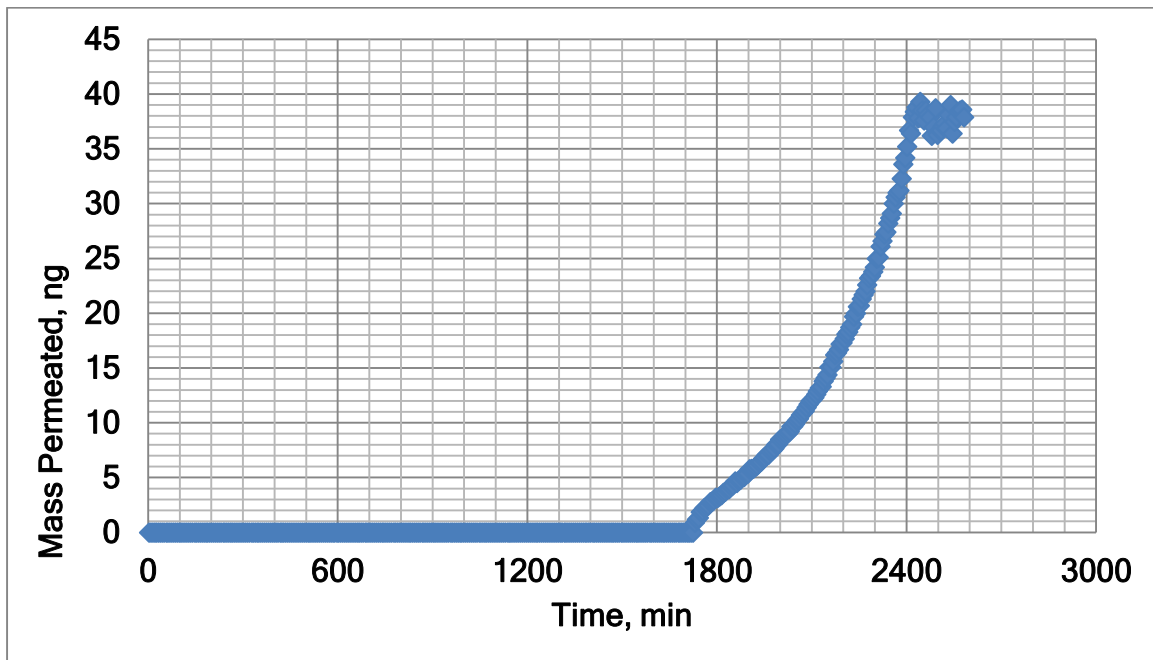

3.3.5   Thickness versus Breakthrough Time Extrapolation: Non-Welded

An objective of the study was to extrapolate permeation breakthrough times from thinner HDPE specimens to 250 mil, which is approximately the full thickness of the candidate container. Containment without breakthrough for 1–2 years might be considered a useful result. The thickness and breakthrough time results are summarized in Table 3. The first column identifies the test number; the swatch identification number is listed in the next column; and the measured swatch thicknesses are listed in the third column. The minimum thickness rather than the mean thickness was selected for initial correlation with breakthrough time because the thinnest spot should have permeated first. The time the liquid was deposited in the swatch (the spike time) and the time to breakthrough are reported. The time to breakthrough includes the date whenever the time was over 1 day duration. Permeation times were calculated and are listed in the "Breakthrough Time" column. The test identification is reported in the last column and consists of the test date.

The variability of the swatch thickness values for only the swatches tested is summarized in Table 4. A full characterization of the entire set of swatches is published separately (*1*).

Table 3. Thickness versus Permeation Breakthrough Time for HDPE at 120 °F: Non-Welded

| No. | Swatch No. | Thickness (mil) | | Time (hours) | | Breakthrough Time (min) | Test ID and Date |
		Nominal	Measured Minimum	Spike	Break-through*		
1	17	20	19.68	1453 (est.)	1622	89	14-04-02
2	17	40	40.91	1006	1856	530	14-04-09
3	4	60	60.75	1419	0240 04-30	740	14-04-29
4	1	80	80.07	1033	0843 04-16	1329	14-04-15
5	2	80	79.82	1025 (est.)	1505 04-26	1720	14-04-25

*Time of breakthrough includes the date when durations were greater than 1 day.

Table 4. Within-Swatch Thickness Variability for HDPE Swatches
Selected for Permeation Testing (*1*): Non-Welded

Swatch No.	Rank	Range Rank	Range (mil)	95% CI Rank	95% CI	Minimum Rank	Minimum	Mean Rank	Mean
17	3	17	1	1	0.111	17	19.68	8	20.38
17	17	4	2.20	1	0.221	14	40.91	13	41.38
4	11	4	1.3	8	0.134	3	60.75	7	61.26
1	4	1	0.9	10	0.098	12	80.07	12	80.74
2	2	2	0.85	9	0.092	5	79.82	13	80.32

Given that the purpose of this study was to predict permeation breakthrough time at 1–2 years, the thicknesses versus breakthrough times were extrapolated based on a Fick's law correlation, and the results are presented in Figure 23. Values for nominal thickness and breakthrough time from Table 3 were used for the correlation. The plot contains the thickness on the *x* axis and breakthrough time on the *y* axis. The Fick's law plot is linear with an adequate correlation coefficient of 0.95.

Solving the regression equation for 250 mil (a full-size container wall thickness) yields a breakthrough time of 10.3 days. The conversion from the square-root value in minutes to the linear value in minutes, hours, and days is described in the Figure 23 caption. Conversely, the regression equation was solved to estimate the thickness required to prevent breakthrough until 365 days. The result was 1491 mil; therefore, a container of about 1.5 in. thickness would be required.

Values corresponding to the 40 mil data point gave the appearance of defect penetration rather than permeation via diffusion, suggesting the possibility of omitting this point from the correlation. On the other hand, there was considerable lag time, which is similar to a typical permeation curve. Inspecting the plot in Figure 23 reveals that the 40 mil data point falls near the regression line. Therefore, omitting the point would have little influence on the extrapolated values of breakthrough time or thickness for breakthrough at 1 year.
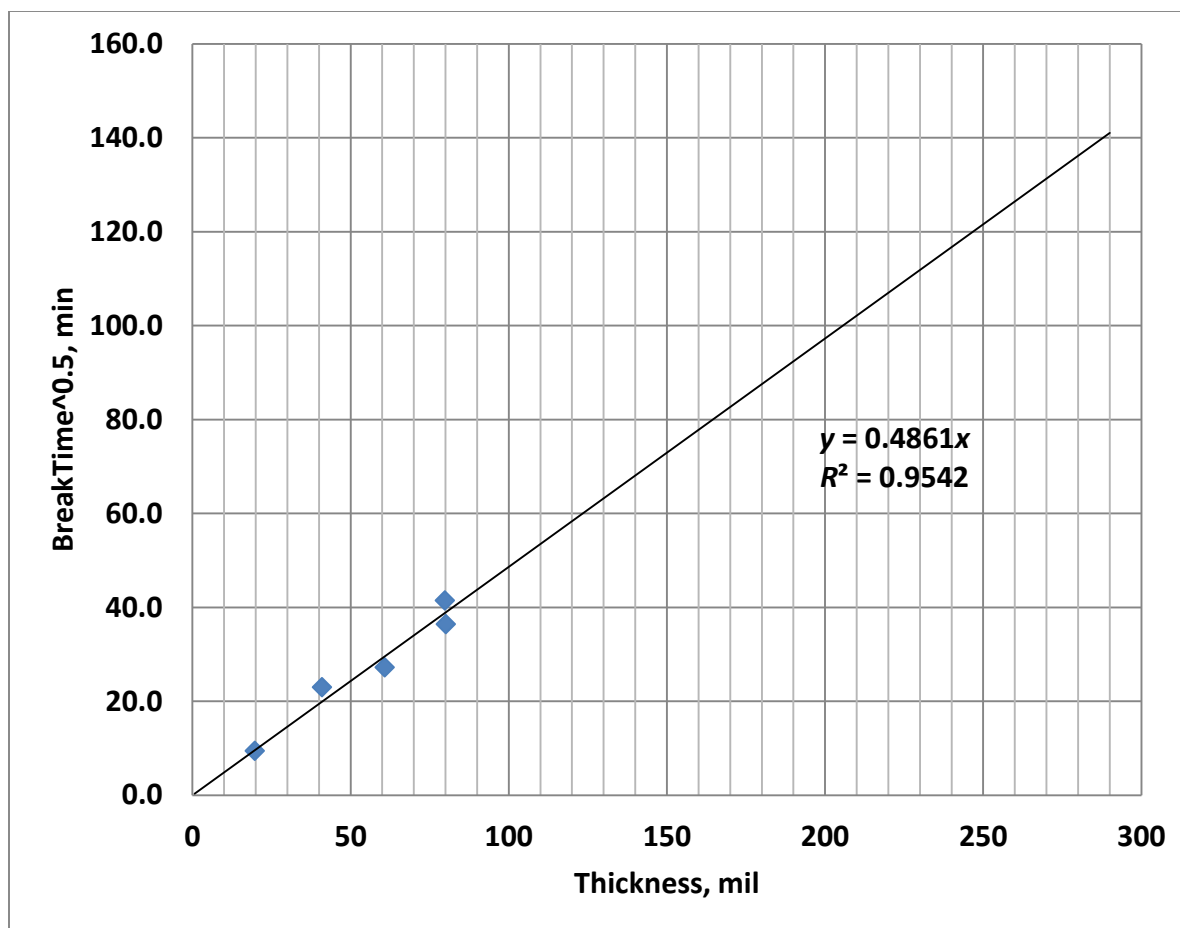
Figure 23. Fick's law applied to plot of thickness vs HD breakthrough time for HDPE with extrapolations to 250 mil; non-welded; $121.5 \text{ min}^2 = 14{,}768$ min or 246 h or 10.3 days; 365 days = 1491 mil or ~1.5 in.

3.3.6   Alternative Correlations: Non-Welded

Alternative correlation calculations are possible. The Fick's law exponent on time is exactly 0.50 (shown in Table 5, in bold); on thickness, it is 2.0. This exponent could be used as a regression-fitting parameter. The correlation coefficient as a function of the Fick's law exponent was calculated at higher and lower values from 0.45 to 0.55 and compared with the theoretical 0.50 exponent value. The results are tabulated in Table 5, nos. 1–7, and are plotted in Figure 24. The correlation coefficient increased marginally at slightly higher values of the exponent and maximized at 0.52 (correlation coefficient of 0.9552, shown in bold in Table 5). Therefore, the theoretical 0.50 exponent was retained.

The correlation presented used an intercept set at zero, which indicated a reasonable zero time to permeate a thickness of 0 mil. However, another alternative correlation consists of not setting the intercept to zero; this provided a small and insignificant increase in the correlation coefficient, which is reported in Table 5, no. 8.

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Table 5. Alternative Regression Correlations and Their Influence on Regression Parameters and Extrapolated Values: Non-Welded

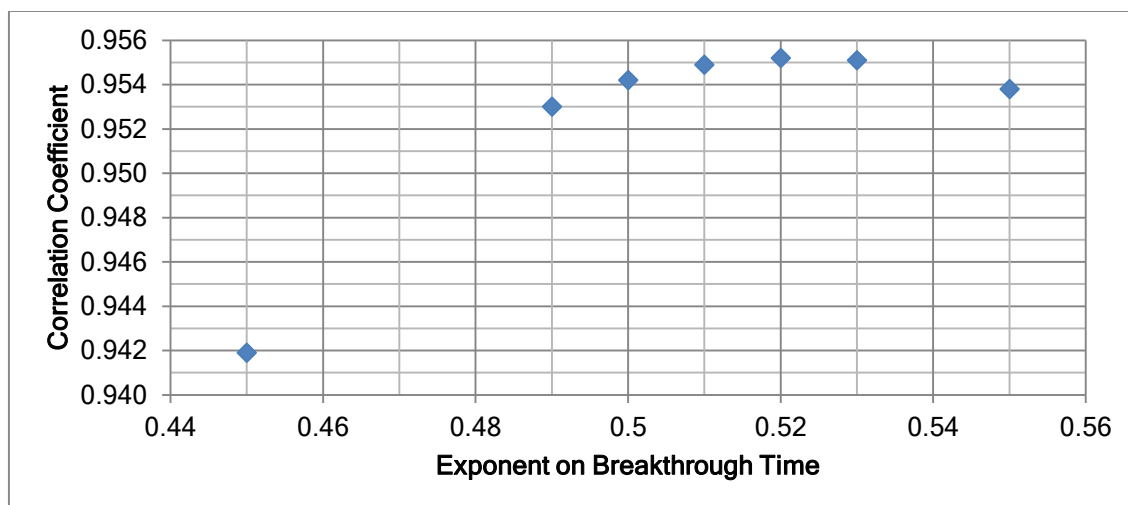| No. | Exponent | | | Slope | Correlation Coefficient | Time$^{0.5}$ (min) | 250 mil Breakthrough Time (days) | 1 Year Container Thickness (mil) |
	Alternative	Breakthrough Time	Thickness					
1	0.45	0.45	2.22	0.342	0.9419	7,319	5.1	2,119
2	0.49	0.49	2.04	0.453	0.9530	12,831	8.9	1,600
3	**0.50**	0.50	2.00	0.486	0.9542	14,768	10.3	1,491
4	0.51	0.51	1.96	0.522	0.9549	16,998	11.8	1,390
5	0.52	0.52	1.92	0.560	**0.9552**	19,565	13.6	1,296
6	0.53	0.53	1.89	0.600	0.9551	22,523	15.6	1,208
7	0.55	0.55	1.82	0.691	0.9538	29,843	20.7	1,049
8	0.50 (Intercept = 1.201)	0.50	2.00	0.468	0.9559	13,683	9.5	1,549
9	1.0	1.0	1.0	16.84	0.818	NA	3.9	31,211

NA, not applicable.

Figure 24. Fick's law: exponent vs correlation coefficient: non-welded.

The working hypothesis for the study was that the thickness dependence should follow Fick's law. A comparison provided in Table 5, no. 9 shows that the correlation coefficient for a linear model is 0.818; this is considerably weaker than the higher correlation coefficient of 0.954 for the Fick's law correlation. The linear model leads to extrapolations to unreasonable values, such as a 3.9 day breakthrough time for a 250 mil HDPE thickness and a 365 day container-thickness requirement that is many times higher than the actual container thickness.

Included in the last two columns of Table 5 are the extrapolated values for estimated days required to reach breakthrough of the full 250 mil thick HDPE container. The various alternative equations yielded a difference of 2–3 days, which is a large relative difference. However, 3 days is inconsequential compared with the target of 365 days. Likewise, the extrapolated estimate of the number of mils required for a container thickness to retard breakthrough to 365 days varied by up to 300 mil, but this is inconsequential compared with the 1500 mil container thickness that is required to prevent breakthrough for 365 days (the 1 year target). The variability of extrapolated values for slight changes in the correlation equation is a usual consequence of the extended extrapolation from 20–80 mil to 250 mil, or threefold the thickness level tested.

Figure 25 is a comparison between the experimental thickness and the breakthrough data as well as the idealized Fick's law plot of the calculated thickness versus the breakthrough time relationship that would be required to yield breakthrough at 365 days for a 250 mil HDPE thickness. The regression equation shown in the figure is for the idealized Fick's law plot. From the figure, it is clear that the permeation resistance of HDPE to HD was too low to meet the target container life of 1 year.
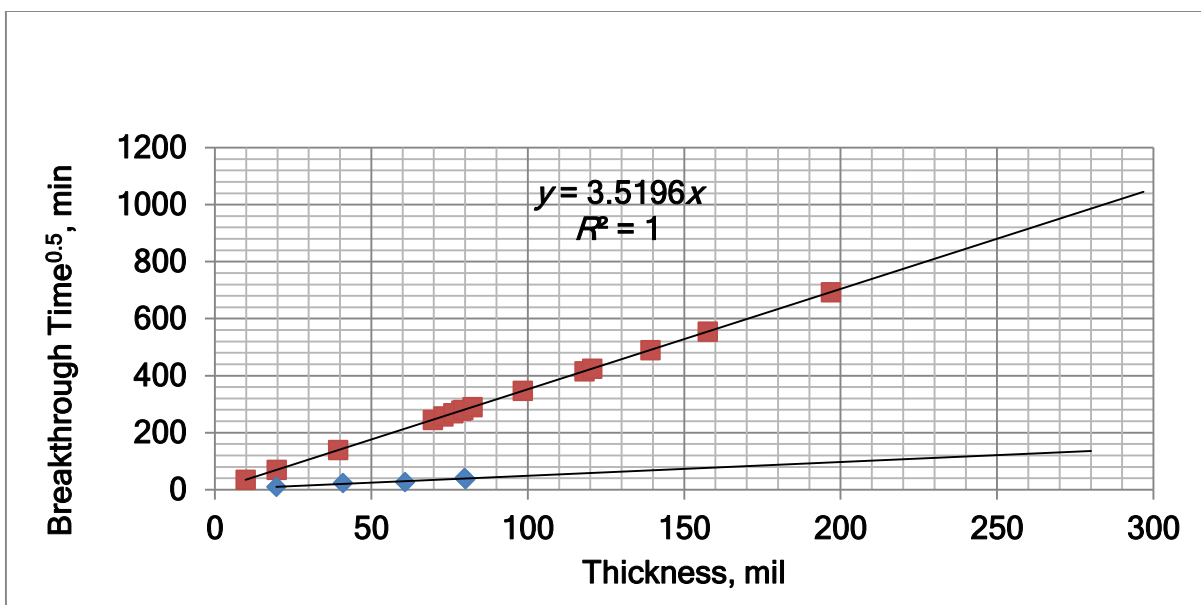
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Figure 25. Idealized Fick's law plot of thickness versus breakthrough time (red boxes; top line) with a plot of experimental data (blue diamonds; bottom line): non-welded.

4.   CONCLUSIONS

Permeation breakthrough measurements for HD and non-welded HDPE at 120 °F were completed over a range of 20–80 mil thickness with the intent of extrapolating to the ~250 mil container thickness. A Fick's law extrapolation inferred a 250 mil breakthrough time of 10–11 days for the non-welded HDPE at 120 °F.

Permeation breakthrough measurements for the welded HDPE at a nominal 20 mil thickness at 100 °F resulted in breakthrough at about 6 h, and the plotted data displayed a molecular permeation curve shape. A confirmation permeation test with a color-change detection method resulted in a breakthrough time of about 8 h, which confirmed the breakthrough time recorded with the more-sensitive detector.

It is unlikely that a 250 mil thick HDPE container will provide safe containment for the target 1 year period.

A custom methodology was developed for the long permeation periods. In addition, the expected breakthrough time and, therefore, test time was completely unknown, and a wide spectrum of test times had to be included in the experimental plan. Given the lack of exploratory data, a strategy was devised based on an idealized Fick's law model with a hypothetical breakthrough time of 365 days for a full container thickness of 0.25 in. This strategy allowed for the selection of swatch-thickness values relevant to the target permeation resistance of the container. This strategy can be recommended for similar problems. The experimental methodology developed was successful in providing the necessary measurements. This methodology for long test periods provides a new capability in permeation cup testing.

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3.   *AVLAG System 4 Technical Manual.* Permeation and Analytical Solutions Branch, Engineering Test Division, Engineering Directorate; U.S. Army Edgewood Chemical Biological Center: Aberdeen Proving Ground, MD, January 2012.

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6.   *Standard Practices for Evaluating the Resistance of Plastics to Chemical Reagents*; ASTM D543-14; ASTM International: West Conshohocken, PA, 2014. UNCLASSIFIED Standard.

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ACRONYMS AND ABBREVIATIONS

AVLAG	Aerosol-Liquid-Vapor Assessment Group
CAS	Chemical Abstracts Service
$CDCl_3$	chloroform, deuterated
CI	confidence interval
CMS	Chemical Monitoring System
CWA	chemical warfare agent
FPD	flame photometric detector
HD	distilled mustard
HDPE	high-density polyethylene
mil	unit equal to 0.001 in.
PAST-1	Permeation and Analytical Solutions Branch
QC	quality control
R^2	regression coefficient
SD	standard deviation
S/N	serial number
UMSC	Universal Munitions Storage Container

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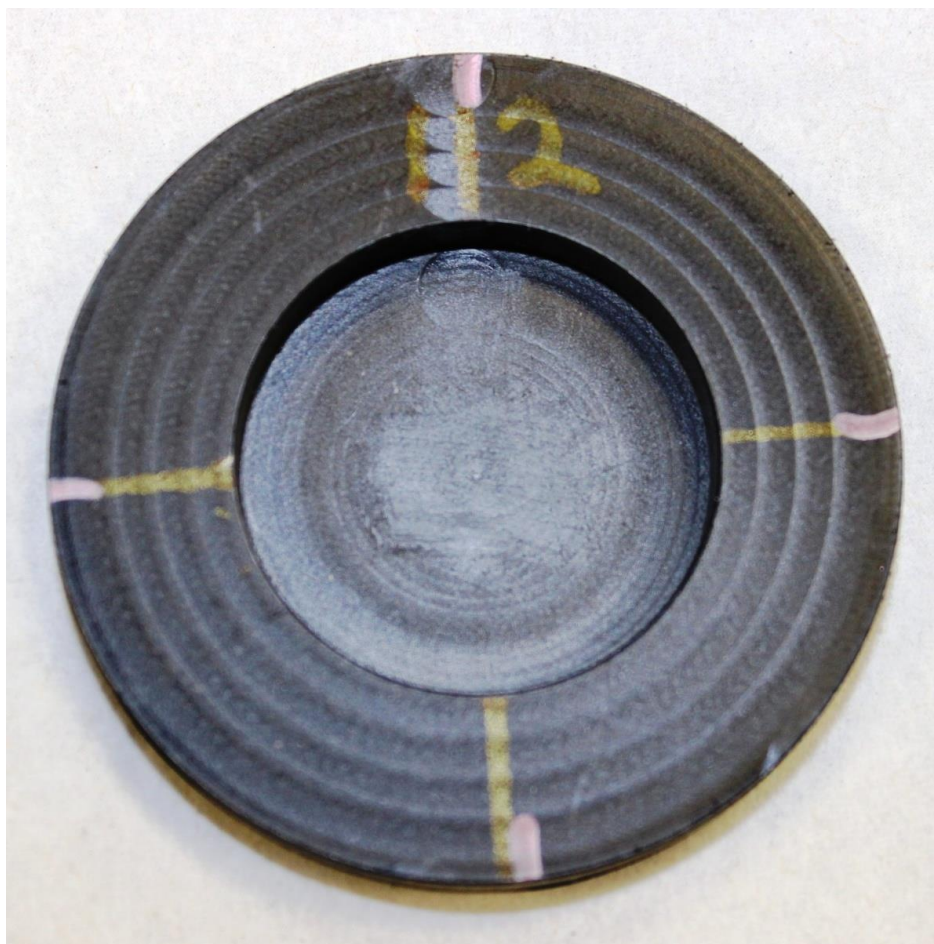**APPENDIX: PHOTOGRAPHS OF PERMEATION SPECIMENS**

Figure A1. Photograph of a high-density polyethylene permeation specimen with end-mill machined well to contain chemical permeant (top view; 12 o'clock is marked).
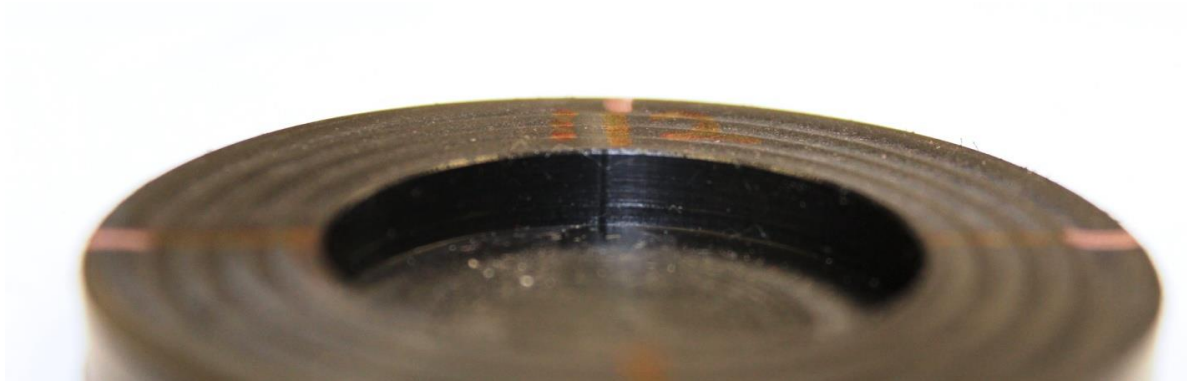

Figure A2. Photograph of a high-density polyethylene permeation specimen with end-mill machined well to contain chemical permeant (side view with focus on interior edge).

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